To my parents
ACKNOWLEDGMENTS

I would like to thank my advisor, Prof. Michele Viola Myers, for providing me with an opportunity to work in her group and offering constant guidance, support and encouragement during my PhD. I would also like to thank her for the innumerable scientific discussions that we had during the course of my study. I would also like to express my gratitude towards my other committee members, Prof. Benjamin Keselowsky, Prof. Malisa Sarntinoranont, Prof. Luisa Dempere and Prof. Christopher Batich for their contributions and their trust in my ability to perform this research.

I was also lucky to have wonderful group members who provided a very friendly and cordial atmosphere in the lab. I would like to thank Derek Hsu, Zachary Bryan, Hunter Henderson, Charles Fisher, Fatmata Barrie, Glenn Bean, Billy Valderama, Ida Berglund, Ryan Hooper and Jack Tilka for the numerous thought provoking discussions and helpful suggestions throughout my PhD. I wholeheartedly thank my friends Prateek, Reno, Tejas, Sambhav, Sid, Aniket, Tara, Isis, Alexa, Amber and others who I may have missed, for keeping me entertained throughout my stay in Gainesville as well as for providing support and encouragement at times of need. Their presence in my life greatly helped me on the long and hard road to PhD.

Last but not the least, I would like to thank my family – my father Mr. Nachhattar Singh, mother Harjit Kaur, sister Manpreet Kaur and brother Gurpreet Singh. Without their unwavering guidance and support, this work would never have been possible. My parents instilled in me the virtues of honesty, humility, hardwork and patience and stood by me through the ups and downs of my life. I can never be able to pay back their debt of unconditional love and care, and this work is dedicated to them.
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<td>Al</td>
<td>Aluminum</td>
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<tr>
<td>Gd</td>
<td>Gadolinium</td>
</tr>
<tr>
<td>ΔG</td>
<td>Gibbs Free Energy</td>
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<tr>
<td>H₂</td>
<td>Hydrogen Gas</td>
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<tr>
<td>HA</td>
<td>Hydroxyapatite</td>
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<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
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<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>Magnesium Chloride</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>Magnesium Hydroxide</td>
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<tr>
<td>MgO</td>
<td>Magnesium Oxide</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
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<tr>
<td>OM</td>
<td>Optical Microscopy</td>
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<tr>
<td>P-B</td>
<td>Pilling-Bedworth</td>
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<tr>
<td>PDS</td>
<td>Poly-Dioxanone</td>
</tr>
<tr>
<td>PGA</td>
<td>Poly-Glycolic Acid</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly-Lactic Acid</td>
</tr>
<tr>
<td>RDA</td>
<td>Recommended Daily Allowance</td>
</tr>
<tr>
<td>RE</td>
<td>Rare Earth</td>
</tr>
<tr>
<td>Sc</td>
<td>Scandium</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>Ultra High Molecular Weight Poly-Ethylene</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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<tr>
<td>Y</td>
<td>Yttrium</td>
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DESIGN AND DEVELOPMENT OF SELF-PASSIVATING BIODEGRADABLE MAGNESIUM ALLOYS USING SELECTIVE ELEMENT OXIDATION

By

Harpreet Singh Brar

May 2012

Chair: Michele Viola Myers
Major: Materials Science and Engineering

Metallic biomaterials such as stainless steels, titanium alloys, and cobalt-chromium alloys have been used as structural implant materials for many years. However, due to their limitations in temporary implant applications, there has been increased interest in the development of a biodegradable structural implant device. Magnesium (Mg) alloys have shown great potential as a material for biodegradable structural implant applications. However, low strength and high degradation rate of Mg under physiological conditions are major limitations, causing the implant to lose its structural integrity before the healing process is complete.

The main aim of this work was to investigate the possibility of designing Mg-based alloys with ability to form selective protective oxides, thereby aiding in the reduction of the initial degradation rate. A thermodynamics-driven design was utilized to select three elements, namely Gadolinium (Gd), Scandium (Sc) and Yttrium (Y), due to the low enthalpy of formation associated with their oxide species. First, binary alloys were cast under inert atmosphere, solution treated and investigated for degradation rate in Hanks' solution. The Mg-Gd binary alloy showed the fastest degradation rate whereas the Mg-Sc binary alloy showed the slowest degradation rate. The degradation of Mg-Gd and
Mg-Y was 18 and 5 times faster than Mg-Sc alloy, respectively. The microstructural analysis of the alloys was performed using X-ray Diffraction (XRD), Optical Microscopy (OM) and Scanning Electron Microscopy (SEM). It was observed that the grain size of Mg-Sc alloys is significantly smaller than Mg-Gd and Mg-Y alloys and can be a contributing factor to the reduction in degradation rate. The hardness behavior of the alloys was also investigated using Vickers microhardness Testing.

To understand the oxidation behavior and kinetics, samples were oxidized in pure oxygen environment and investigated using microstructural and thermogravimetric analysis (TGA). Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were also used to characterize the chemistry of the surface oxides. Selective oxidation of the alloying species was observed on the surface of all the alloys, indicating a strong driving force for their formation out of solid solution Mg. The degradation rate of the oxidized samples was also investigated in Hanks’ solution and compared with the rate of freshly polished samples. The oxide formation on Mg-Y alloys was found to be most protective as it reduced the degradation rate by more than 50%. On the other hand, oxidized Mg-Sc samples did not show any appreciable decline in degradation rate as compared to polished samples.

Based on the information gathered from the binary alloys, ternary alloy system was selected. The thermodynamic and empirical models were applied to predict the properties of the alloy. The models were validated using the techniques mentioned above. It was observed that the predictions matched with the experimental results.
CHAPTER 1
INTRODUCTION

1.1 Motivation

Advances in the field of medical science over the last century have significantly improved the life expectancy of people around the world. According to the US Census Bureau, 1 out of every 5 people in US will be over 65 years of age by the year 2030. Additionally, 80% of the people above the age of 65 have at least one chronic condition [1]. Hence, the increasing aging population and the desire for an active lifestyle create a driving force for the high performance biomedical implant materials. Orthopedic and cardiovascular implants constitute the two major sectors of the medical implant industry. The global market for orthopedic devices was an estimated $31.6 billion in 2007 and the cardiovascular stent market stood around $5 billion [2].

Metallic materials play an important role as biomaterials for load bearing applications such as stents and orthopedic implants. Of the total number of orthopedic operations performed per year in the United States, open reduction of fracture and internal fixation are the most common ones [3]. Traditional implant materials like stainless steel, titanium alloys and cobalt-chromium alloys are designed to stay in the body permanently. They are intended to remain neutral in-vivo and not interact with the body [4]. However, long-term presence of the implant materials has its own specific drawbacks. In coronary stents, for example, bare metal stents can lead to thrombogenicity, restenosis, physical irritation, inflammatory local reactions and mismatch in the mechanical behavior of the stented and non-stented vessel areas [5]. Development in the drug-eluting stents have reduced the incidence of restenosis, the other problems however, still persist. Similarly, use of permanent implants like screws
and plates for securing serious fractures also have their side effects. Secondary surgeries maybe required to remove the implants once the bone is healed, thereby increasing the cost of treatment and patient morbidity [6]. Additionally, the difference in the modulus of the present implant materials and the bone can cause stress-shielding effects, leading to reduction in strength of the healed tissue [7, 8].

Biodegradable materials have the possibility of providing more physiological repair, with temporary, limited support and better tissue growth. Polymers were the first materials to be commercially used for biodegradable and bioabsorbable applications with poly-glycolic acid (PGA), poly-lactic acid (PLA) and poly-dioxanone (PDS) being the earliest adopted and most commonly used absorbable materials [9]. The use of biodegradable polymers in load bearing applications has been mainly limited by their low strength, as a large amount of material is be needed to attain the strength required for load bearing applications. Metals on the other hand, have desirable mechanical properties like high strength and fracture toughness. However, most of the metals are either non-biodegradable or show toxicity to human body. Corrosion products of conventional metallic implant materials like stainless steel, cobalt chromium and nickel-based alloy have been shown to be harmful to human body [10-13]. This need for a biodegradable material with improved mechanical properties and the ability to degrade in the body without releasing any harmful byproducts has lead to increased research interest on magnesium (Mg) and its alloys.

Magnesium is an exceptionally lightweight material with high specific strength [14]. It is one of the most reactive metals and degrades under physiological conditions [15], thereby providing an opportunity to develop it into a biodegradable implant material for
load bearing applications. Additionally, its elastic modulus and strength are closer to the natural bone than other commonly used metallic implants [16]. Table 1-1 compares the mechanical properties of bone and various materials being used for implant applications.

Despite all these advantages, Mg has certain limitations like low strength and high degradation rate that pose a challenge in its use as a structural implant material. These limitations can be alleviated by addition of alloying elements to pure Mg or through use of surface coatings [16-18]. However, alloy chemistry strongly drives microstructural evolution and desired properties often need conflicting complex microstructural features, making it difficult to find a balance of the properties by using a traditional, edisonian-type approach otherwise known as “trial-and-error”. This work was performed with a focus on designing biocompatible Mg alloys that is capability of growing a selective “designer” protective oxide for implant applications using systems design approach. Emphasis was given on utilizing a systematic approach to find a balance between the properties required for implant applications and optimizing the overall performance of the alloys.

1.2 Magnesium as a Potential Biomaterial

Magnesium is the second most abundant element involved in cellular structures and is the fourth most abundant cation in human body. The body of an average adult contains around 21-28 g Mg, with more than half of it stored in the bones [19]. Mg is an essential element for human metabolism as it acts as a cofactor for many enzymes and stabilizes the structure of DNA and RNA. The US recommended daily dietary allowances (RDA) for Mg are 320 mg/day for women and 420mg/day for men [20]. Deficiency of Mg has been linked to various diseases like osteoporosis, decreased
membrane integrity and function, increased risk of cardiovascular problems like cardiac arrhythmias, vasoconstriction of coronary arteries, increased blood pressure and accelerated aging [21]. Studies have also indicated the possibility of stimulatory effects of Mg on the growth of new bone tissue due to its functional role and presence in bone [22, 23]. It binds strongly to phosphates, thereby influencing the mineralization of bony tissue by its control of hydroxyapatite (HA) formation. As a result, Mg is often seen in dietary supplements and drugs. As compared to other metal ions, human body can accommodate higher amounts of Mg concentration levels in serum, with hypotension and respiratory distress occurring at levels exceeding 1.05 mmol/L [19]. In addition, the concentration of Mg in human body is efficiently controlled by homeostatic mechanism and excess Mg excreted in urine, thereby making the incident of Mg toxicity extremely rare [19].

In addition to its biocompatibility, Mg also has desirable mechanical properties. It is an exceptionally lightweight metal and has a specific density of 1.74 g/cm³, making it 1.6 and 4.5 times lighter than aluminum and steel respectively [16]. Furthermore, its density is similar to that of bone (1.8-2.1 g/cm³) [16]. The specific strength of Mg is higher than conventional metallic implants, thereby reducing the amount of material required for a given load application. As shown in Table 1-1, the elastic modulus of Mg (45 GPa) is closest to that of human bone when compared to other metallic implant materials. This helps in reducing the modulus mismatch between the bone and the implant, thereby reducing the stress shielding effect and improving the bone strength.

Mg is also one of the most reactive metals of the periodic table. In aqueous environments, Mg dissolution generally proceeds by an electrochemical reaction with
water to produce magnesium hydroxide (Mg(OH)₂) and hydrogen gas (H₂) [24]. The overall reaction of Mg dissolution in water can be written as:

\[ \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \] (1-1)

The overall reaction stated above can also be expressed as a sum of following partial reactions [17]:

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \text{ (anodic reaction)} \] (1-2)

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \text{ (cathodic reaction)} \] (1-3)

\[ \text{Mg}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \text{ (product formation)} \] (1-4)

The rate of degradation reaction depends on various factors like pH, solution composition, alloying elements, microstructure and presence of proteins. Figure 1-1 shows the Pourbaix diagram for Mg-H₂O system at 25°C [25]. It can be seen that under the physiological conditions of pH (7.2-7.4), Mg undergoes corrosion to produce Mg(OH)₂. Furthermore, presence of chloride ions in physiological media reduce the efficiency of Mg(OH)₂ as they convert it to magnesium chloride (MgCl₂), which has a higher solubility. This leads to increased corrosion attack on Mg [17].

1.3 Historical Use of Magnesium as a Biomaterial

The first reported use of Mg as a biomaterial was by physician Edward C. Huse who used Mg wires as ligatures to stop bleeding vessels of 3 patients in 1878. He observed and documented the degradable properties of the material and the dependence of degradation time on the size of Mg wire used [26]. Austrian physician Erwin Payr started his first experiments on Mg resorption in 1892 [27]. In 1900, he performed in-vivo experiments on pigs and the femoral arteries of the dogs using vessel connectors made of Mg [27, 28]. Albin Lambotte and his assistant Verbrugge used Mg
for osteosynthetic application for the first time in 1906 when they used Mg plate with 6 steel screws to stabilize a fracture on the tibia [29]. However, the implant degraded rapidly and resulted in extensive subcutaneous gas cavities, local swelling and pain to the patient. The small fragments of the Mg plate were left after 8 days and were retrieved. He concluded that the extensive dissolution of Mg took place due to the electrochemical reaction between Mg plate and the steel screws [29]. After further investigation and animal studies [30], he continued using Mg screws and plates for healing fractures in children [30, 31]. Based on his new encouraging results, he recommended using Mg without combining it with other elements to prevent galvanic corrosion [30]. Concurrently to Lambotte’s studies, critical reports on the use of Mg as implant material in bone applications were also published. The major concerns in these studies were the production of abscess gas cavities and rapid degradation of Mg [32, 33]. Troitskii and Tsitrin published one of the most extensive studies on the use of Mg alloys for osteosynthetic application in 1948. They reported the use of plates and screws made of Mg-Cd alloy to treat of 34 cases of pseudoarthrosis in humans [34]. There were 9 failures out of the 34 cases, which were attributed to infection or other factors. The corrosion process released hydrogen, which was drawn off using subcutaneous needles. No inflammatory responses or increase in serum levels of Mg was observed, and most of the implants maintained their mechanical integrity for about 6-8 weeks [34].

With improvements in corrosion protection, there has been a renewed interest in use of Mg for biodegradable implant applications. The most significant achievement of Mg as biomaterial has come from the use of Mg alloy as biodegradable coronary stents.
Heublein and colleagues conducted the pioneering investigations on the suitability of AE21 alloy containing 2% aluminum (Al) and 1% rare earth metals as a biodegradable stent in porcine model [5]. The implantations demonstrated very low thrombogenic and inflammatory responses. Subsequently, a modified Mg alloy based Absorbable Magnesium Stent (ABS) was developed by Biotronik. The stent was constructed using laser from a single tube of WE43 alloy containing Mg (>90%), Zirconium (Zr) (<5%), Yttrium (Y) (<5%) and other rare earths (RE) (<5%) [35]. Figure 1-2 shows the image of the stent [35]. Initial animal studies in porcine coronary arteries showed promising results and led the way for clinical trials of the stent. Initially, 20 patients with symptomatic critical limb ischemia were treated with ABS [36]. The preliminary analysis after stent implantation did not show any evidence of toxicity. A 3-month follow up showed 89.5% primary clinical patency and no major amputation was required [36]. The positive results of this study resulted in initiation of first coronary clinical study. In this study, WE43 stents were implanted in 63 patients with anginal symptoms and single de novo lesions. Though the stents showed good initial results, final cross section area of the vessel was smaller than the non-biodegradable stents. This was attributed to the early recoil as the stent completely degraded after 4 months [37].
Table 1-1. Summary of mechanical properties of natural and implant materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Strength (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Biodegradable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Materials</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Collagen</td>
<td>60 b</td>
<td>1 b</td>
<td>Yes</td>
</tr>
<tr>
<td>Cortical bone</td>
<td>100-200 b</td>
<td>10-20 b</td>
<td>Yes</td>
</tr>
<tr>
<td>Inorganic Materials</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>185-232c</td>
<td>41-45d</td>
<td>Yes</td>
</tr>
<tr>
<td>Stainless Steels</td>
<td></td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>Cobalt Alloys</td>
<td>655-1400 b</td>
<td>195-210 b</td>
<td>No</td>
</tr>
<tr>
<td>Titanium Alloys</td>
<td>550-985 b</td>
<td>100-105 b</td>
<td>No</td>
</tr>
<tr>
<td>Platinum Alloys</td>
<td>152-485 b</td>
<td>147 b</td>
<td>No</td>
</tr>
<tr>
<td>Synthetic Hydroxyapatite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-PLA</td>
<td>28-50 a</td>
<td>1.2-3 a</td>
<td>Yes</td>
</tr>
<tr>
<td>D,L-PLA</td>
<td>29-35 a</td>
<td>1.9-2.4 a</td>
<td>Yes</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>39-40 b</td>
<td>0.94-1.05 b</td>
<td>No</td>
</tr>
</tbody>
</table>

*a*Indicates compressive strength (MPa)

(c) [Smithells CJ, Gale WF, Totemeier TC, 2004. Smithells metals reference book. Amsterdam (various pagings)]
(d) [Staiger MP, Pietak AM, Huala ma J, Dias G, 2006. Biomaterials Vol. 27 Pages 1728-34]
Figure 1-1. Pourbaix diagram for the Mg-H₂O system at 25°C [Adapted from Marcel Pourbaix, 1966. Atlas of Electrochemical Equilibria in Aqueous Solutions]

Figure 1-2. Photograph of the tubular slot balloon expandable WE43 alloy stent [Reprinted with permission from John Wiley and Sons, 2004. Journal of Interventional Cardiology Vol. 17 (Pages 391-395, Figure 1)]
2.1 Corrosion of Magnesium and its Alloys

Currently, there is a significant effort to investigate various different alloys for structural biodegradable implant materials. The high chemical activity of Mg allows it to corrode in aqueous environment, thereby making it a potential candidate for biodegradable applications. However, it is this very ability of Mg to corrode in an aqueous environment that is also one of the biggest hurdles in its use as an implant material. Under physiological conditions, the corrosion rate is too rapid and the implants tend to lose their structural integrity before the tissue is properly healed, thereby leading to implant failure. It is therefore very important to improve and control the corrosion properties of the Mg alloys so that they can be used for biodegradable applications. This section focuses on the thermodynamics of pure Mg, strengthening mechanisms, oxidation behavior and surface films, and the effect of microstructure on the corrosion and oxidation of Mg alloys.

2.1.1 Thermodynamics of Magnesium Corrosion

In order to understand the corrosion behavior of Mg and its alloys, it is vital to understand the thermodynamic stability of pure Mg and its compounds in various environments. This information can provide a valuable insight into the corrosion behavior of Mg and enable predictability of its behavior in those environments.

As compared to other structural materials, Mg has the lowest standard electrochemical potential, as shown in Figure 2-1. Pure Mg (Mg\(^{2+}/\text{Mg}\)) in contact with solution containing Mg\(^{2+}\) ions at 25°C has an electrode potential of -2.37 \(V_{\text{nhe}}\) [24]. However, for practical purposes, actual corrosion potential of Mg in contact with dilute
chloride solutions is -1.7 V_{nhe} [24]. This difference between the theoretical standard potential and actual corrosion potential is due to the formation of surface film of Mg(OH)\(_2\) or MgO [24].

Due to its reactivity, Mg has a strong driving force for oxidation. Under natural environments, Mg spontaneously transforms into its oxidized states. The driving force for these oxidation reactions is the reduction in Gibbs free energy (\(\Delta G^\circ\)) as mentioned below [17]:

\[
\begin{align*}
\text{Mg} + 2\text{H}_2\text{O} & \rightarrow \text{Mg(OH)}_2 + \text{H}_2 & \Delta G^\circ = -359 \text{ kJ/mol} \\
\text{Mg} + \frac{1}{2}\text{O}_2 & \rightarrow \text{MgO} & \Delta G^\circ = -569 \text{ kJ/mol} \\
\text{Mg} + \text{O}_2 + \text{H}_2 & \rightarrow \text{Mg(OH)}_2 & \Delta G^\circ = -833 \text{ kJ/mol}
\end{align*}
\]

As a result of the thermodynamic driving forces, exposure of Mg to environments containing oxygen or water results in the formation of oxides or hydroxides on the surface [40, 41]. The stability of the oxidized states of Mg over its metallic state is also supported by the thermodynamic data of the Mg compounds and species as shown in Table 2-1. The more negative the chemical potential, the more stable the species is compared to others in the media. From the data in Table 2-1, it can be seen that corrosion of Mg is a spontaneous process as Mg\(^{2+}\), MgO and Mg(OH)\(_2\) have more negative potentials. The final product formed depends on the media to which Mg is being exposed. It can be further noted that since chemical potential of Mg(OH)\(_2\) is more negative than MgO, exposure of Mg to aqueous solutions will lead to the preferential formation of Mg(OH)\(_2\). This transformation of Mg to its hydroxide proceeds according to Equation 2-1, releasing \(\text{H}_2\) as a byproduct.
Pourbaix diagram and other E-pH diagrams can be used to predict the theoretical stability of Mg in water. The pourbaix diagram of Mg and pure water is shown in Figure 1-1. It is known that Mg has the tendency to be oxidized into ions, oxides or hydroxides in most of the E-pH regions, resulting in a very large corrosion domain.[14, 17, 25, 42]. Surface passivity is only possible in the narrow negative potential region and high alkalinity region (pH > 10.5). Under high pH conditions, even though Mg(OH)$_2$ forms as the corrosion product film on the surface, it does not provide complete protection since it is semi-protective in nature [43]. On the other hand, the negative potential required for immunity is also significantly more negative than its equilibrium potential. As a result, even though the self-passivity of Mg is theoretically possible, most of the common solutions do not fulfill the requirements for passivity.

Though the E-pH diagrams help us understand the activity and passivity of Mg surface, they have some limitations. These diagrams offer limited information on the kinetics of the corrosion process and only predict the thermodynamic stability or driving force for corrosion. Magnesium corrosion has been shown to be highly dependent on the kinetics [17]. Another limitation of the E-pH diagrams is that they assume uniformity of substances or phases. In practical systems this is seldom true, as variations in the concentration of ions, pH and phases exist. Also, typical E-pH diagrams do not take into account the effect of chemical composition of the solution or the presence of aggressive species in the solution. Hence, extreme care should be taken while using these diagrams to attempt corrosion prediction in solutions other than water.
2.1.2 Oxidation Behavior and Surface Film Formation

2.1.2.1 Oxidation of metals

A surface film can be described as a layer of corrosion products formed on the surface in presence of ambient environment. When the ambient environment is oxygen or water rich, the surface film formed constitutes of the metal oxide or hydroxide [17]. Typically, the formation of a surface film is thermodynamically and kinetically spontaneous on the surface of reactive metals. However, the actual oxidation mechanism and reaction path can depend on various factors. Figure 2-2 shows some of the stages and aspects of metal oxidation. The initial step in metal-oxygen reaction on a clean metal surface involves the absorption of oxygen on the metal surface. As the reaction proceeds, the oxygen can dissolve into the metal, leading to the formation of the oxide as a surface film or a separate oxide nuclei. When a continuous film covers the surface, it separates the metal from the gas, and the reaction can proceed only through solid-state diffusion of reactants through the film. Some metals may form scales that are porous in nature, having microcracks and porosity, and even macrocracks. Such scales do not act as solid-state barrier between the reactants. In such cases, the oxide layers are non-protective and may not passivate the surface [44]. The passivity and protective nature of the surface oxide can be experimentally determined by measuring the reaction rate and kinetics of oxidation. One of the methods to do so is thermogravimetry, where the change in the weight of the metal is recorded over time. This data can be used to identify the rate equations, which can then be used to classify the oxidation behavior of the metal [44, 45].
In multi-component alloys, oxidation becomes a complex phenomenon with the inclusion of higher order oxides, different oxygen affinities, and mobilities. However, the oxide with the most negative free energy of formation under oxidation conditions has the highest probability to form preferentially compared to other oxides. Another important aspect is whether the oxide forms as sub-surface precipitates, known as internal oxidation, or as a scale on the surface due to external oxidation. If the outward flux of the selectively oxidized component is substantially smaller than the inward flux of oxygen, internal oxidation takes place.

2.1.2.2 Surface film formation on magnesium

As Mg tends to oxidize or dissolve in most environments, its surface is also covered with a surface film under normal conditions. Additionally, a surface film on Mg can vary in composition and structure based on the alloying additions, environment and formation conditions. In general, the spontaneous surface film formed on Mg in air is relatively thin (approximately 2 nm), though it can grow with time [46]. However, the nature of the surface film on Mg is not very well understood [24].

Based on thermodynamic free energy of formation, the surface film on Mg should consist of MgO in dry environments and Mg(OH)₂ in aqueous environments. However, under normal atmospheric conditions where some amount of water vapor is generally present, surface films on Mg contain both MgO and Mg(OH)₂ [47-49]. Even if the original film is formed under dry conditions and consists only of MgO, under aqueous situations it converts to more stable Mg(OH)₂ as there is a thermodynamic driving force for the reaction [50]. However, it is believed that the microstructure of the surface film is more complex than uniform structure. It has also been reported that even though Mg(OH)₂ layer grows, an ultra thin MgO layer is still maintained at the metal interface.
It has been suggested that the multi-layer structure consists of an outer platelet like structure (Mg(OH)$_2$) and compact layer (MgO) next to the substrate [47].

Other environmental and processing factors can also effect the composition and structure of the surface film. Additional gases present in the environment can also interact with the surface film to change its characteristics. Carbon dioxide (CO$_2$) present in the atmosphere can react with the Mg(OH)$_2$ to produce a hydrated carbonate [43].

Upon immersion in aqueous solutions, the presence of additional ions like chlorides or fluorides can also combine with the film resulting in formation of hydrated salts containing respective ions [17]. The presence of alloying elements in the substrate can also have an effect on the composition of surface film formed. Elements present in the substrate also contribute to the surface film and their oxides and hydroxides can become components of the surface film. The effect of the trace or alloying elements on the surface film depends on the mobility of the ions and their affinity for oxygen. Analysis of the surface films on Mg alloys containing Zn, Al, Y, Mn or Zr have shown the presence of secondary constituents [46, 52, 53]. The ratio of the different ions in the film as compared to substrate depends on the unique affinity of the ions for oxygen, hydroxyl groups and their respective mobility within the substrate and the surface film [17, 54]. In one of the studies, it has been reported that if Al content in the substrate exceeds 4 wt%, it can lead to Al concentration of up to 35 wt% in the inner layer of surface film. Above a critical Al concentration in substrate, a continuous Al$_2$O$_3$ amorphous structure can be formed in the surface film [17].

Despite the ability to form surface films comprising of oxides and hydroxides, Mg does not possess the corrosion resistance comparable to that provided by surface films
of other elements [17]. The lack of protection of the surface films is due to various contributing factors. One of the factors that determine the protective nature of the oxide is the Pilling–Bedworth (P-B) ratio. The P-B ratio is the ratio of the specific volume of a metal oxide to the specific volume of the metal. When this ratio is less than 1, it leads to porous or cracked film, thereby making it inadequate for protection for the substrate.

When the P-B ratio is higher than 1, the film is relatively passivating as it forms a protective barrier between the air and the substrate [55]. Since the P-B ratio of MgO/Mg is less than 1 (0.81), it is often mentioned as a reason for the lack of protective surface film [55]. Under normal dry conditions, the oxide is thin and sufficiently ductile to provide limited protection. However, at higher temperature, the thickness of the oxide increases and it cracks due to small P-B ratio [41, 56]. On the other hand, the lack of corrosion protection in aqueous solutions can not be attributed to P-B ratio as Mg(OH)₂ has a P-B ratio greater than 1. Therefore, there must be another mechanism driving the poor protection of Mg under aqueous solutions. Based on the E-pH diagrams discussed in Section 2.1.1, this can be explained by the electrochemical instability of Mg(OH)₂ in acidic, neutral or mildly basic solutions. Another reason for the lack of corrosion protection has been reported to be the presence of aggressive ion species like Cl⁻. In presence of these ions, Mg(OH)₂ is converted to MgCl₂, which has a significantly higher solubility in water than Mg(OH)₂, leading to an accelerated corrosion attack on the Mg metal [17].

In aqueous environments, the conversion of MgO to Mg(OH)₂ can take place by one of the two potential pathways: (1) hydration of MgO and (2) dissolution of MgO and deposition of Mg(OH)₂. According to the first approach, the oxide is converted to
hydroxide on contact with water. This results in volume change from 14.02 cm$^3$/mol for MgO to 24.33 cm$^3$/mol for Mg(OH)$_2$ [17]. This volume expansion is believed to cause the disruption of the surface film, thereby, leading to the porous and non-protective nature of Mg(OH)$_2$ layer in the surface film [15, 57, 58]. According to the second approach, exposure to aqueous conditions lead to the dissolution of MgO and the Mg substrate and deposition of Mg(OH)$_2$ on the surface due to low solubility of Mg(OH)$_2$ in the solution. The deposited Mg(OH)$_2$ lacks the compactness and thereby, the ability to protect the substrate from corrosion. Therefore, even if there is a compact MgO layer on the surface, it can get partially dissolved and be converted to Mg(OH)$_2$, thereby initiating corrosion. Once the surface film breaks down, its hard for it to repair itself as Mg(OH)$_2$ does not necessarily deposit on the areas of broken surface film. Additionally, the evolution of hydrogen from the dissolution of substrate reduces the chances of a compact layer deposition. All these factors lead to reduced deposition rate of Mg(OH)$_2$ as compared to the dissolution rate, thereby making the self-inhibition of corrosion difficult [17].

2.1.3 Metallurgical Aspects of Corrosion of Magnesium and its Alloys

Corrosion resistance of Mg and its alloys depends greatly on their metallurgy. Metallurgical factors affecting their corrosion are impurities, secondary phases and other microstructural features like grain size and phase distribution [17]. Understanding these factors and their influence on the corrosion can provide a vital tool in reducing the overall corrosion rate of existing alloys and developing new alloys with superior properties.

Galvanic corrosion is an electrochemical process where two components with different electric potentials come in contact with each other in presence of an
electrolyte, resulting in the corrosion of the component that is more electrochemically active. It is one of the most important corrosion phenomenon of Mg alloys as they have high negative corrosion potential and act as anodes when in contact with more passive components. These components can be two different metals in contact with each other or two different phases present in a microstructure. While the former is known as macro-galvanic corrosion, the latter is called microgalvanic corrosion [59, 60]. Microgalvanic activity occurs as some grains, impurities, intermetallic particles etc. act as anodes while others act as cathodes. It has been generally observed that Mg matrix with lower amount of alloying elements acts as micro-anode, and is therefore preferentially corroded. On the other hand impurity particles, secondary phases and intermetallic particles act as micro-cathodes [17, 46, 61]. The following sub-sections discuss the effects of various constituents like impurities, secondary phases and other microstructural features on corrosion.

2.1.3.1 Effect of impurities

Presence of different elements can decrease, increase or have negligible effect on the corrosion resistance of Mg alloys. The elements that are detrimental for the corrosion resistance of Mg alloys are generally termed as impurity elements [24]. There have been various studies to determine this effect on the corrosion resistance [43, 59, 62]. Based on experimental evaluations, iron (Fe), nickel (Ni), cobalt (Co) and copper (Cu) are the most deleterious impurity elements for Mg. These elements were found to have an adverse effect on the corrosion rate even at concentrations less than 0.2% [17, 62]. Subsequent studies have associated the deleterious effect of the Fe, Ni and Cu impurities on the low solid-solubility of these elements in Mg, as they provide active cathodic sites for propagation of corrosion [24, 63, 64]. Another important factor
regarding these impurities is the existence of critical concentration called tolerance limit [24]. At concentrations below this limit, these impurities have minimal effect on corrosion, but above it they accelerate corrosion greatly. Song et. al. have summarized that the impurity effect can be due to two main reasons: 1) accelerated galvanic corrosion of Mg matrix due to general dissolution of Mg alloy and re-precipitation of metallic Fe, Ni and Cu on the alloy surface, thereby actively forming new galvanic coupling sites 2) acceleration of galvanic corrosion when any of the impurity elements Fe, Ni or Cu exceeds its solubility limit in Mg and precipitate as intermetallic phase [65]. Increasing purity of the alloy can effectively eliminate this effect and has been shown to decrease the corrosion rate between 10-100 times [63].

2.1.3.2 Effect of solid solution and secondary phases

Under the conditions of solid solution, there can be a change in the electrical potential of the Mg matrix depending on the concentration of alloying elements. In concentrated binary and ternary alloys, the concentration of alloying elements can vary substantially at the center of the grain to the grain boundary and vicinity of second phase particles [17, 66]. This can make the area with higher concentration of alloying element more passive, and hence increase the anodic/cathodic activity and preferential corrosion of the centre of the grain [67]. However, solid solution has only a minor effect on the corrosion rate in comparison to the effect of secondary phases as most of the alloying elements have significant effect on corrosion only after formation of secondary phases [24].

Almost all the secondary phases in Mg alloys are nobler than the Mg matrix [65, 67-69]. This makes them less susceptible to corrosion as compared to Mg matrix. On the other hand, since they are more inert than the matrix, they can act as an effective
cathode, leading to higher corrosion rate of the Mg matrix [17, 70]. Hence, the secondary phase is shown to have dual influence on the corrosion of Mg alloys, where it can act as a barrier to corrosion and a cathode at the same time. Which of the two influences dominate, depends on the volume fraction and distribution of secondary phases in the matrix. Presence of fine and continuously distributed secondary phase is more effective at inhibiting the corrosion in the alloy as compared to the presence of small and discontinuous secondary phase [17].

2.1.3.3 Effect of grain size

Even though the reduction in grain size is known to improve strength, ductility and wear resistance, there is lack of fundamental understanding of the effect of the grain size on the corrosion behavior of an alloy [71-73]. There is a significant body of literature pertaining to the possible effects of grain size on corrosion behavior but there is little consensus on the exact relationship between corrosion behavior and grain size. One of the major problems associated with understanding the effect of grain size on corrosion resistance of alloys is the difficulty to isolate the effect of grain size from other microstructural changes associated with processes used to obtain different grain sizes [72]. However, for Mg alloys, a consistent trend in the literature can be seen that associates reduction in grain size with increase in corrosion resistance in neutral and alkaline solutions [67, 71, 74, 75]. Formation of a better passivating film on the surface of the fine-grained alloys is said to be one the reasons for superior corrosion protection. Since Mg has a P-B ratio less than 1, increased grain boundary density might decrease the compressive stresses associated and help to compensate for the oxide/base mismatch [72]. This claim has been substantiated by scratch tests [76, 77] and the observation of reduced cathodic kinetics in 0.1 M NaCl [71]. Table 2-2 summarizes the
data found in literature regarding the effect of grain size reduction on the corrosion susceptibility of the alloys.

2.2 Strengthening of Magnesium Alloys

This section focuses on the most significant ways by which the strength of crystalline solids can be increased by restricting the dislocation motion. Different obstacles like solute atoms, grain boundaries, precipitates or dispersions can be employed to inhibit the movement of dislocations and help in strengthening materials. Most of the high-strength materials are hardened by employing one or more of these mechanisms. Various studies have been done to analyze the effects of grain boundary strengthening [78, 79], solid solution strengthening [80, 81] and particle strengthening [82-85].

Grain boundaries provide effective barrier to the dislocation movement, as the crystallographic factors do not permit the passage of dislocation from one grain to adjacent one through the grain boundary. Hall-Petch provided a relationship between the yield point of a material and the grain size as:

$$\sigma_y = \sigma_0 + kD^{1/2}$$ (2-4)

where $\sigma_y$ is the yield strength, $\sigma_0$ is the frictional stress required to move dislocations, $k$ is the Hall-Petch coefficient and $D$ is the grain size [86, 87]. Researchers have provided various theories to explain this relationship [88-90]. One of the accepted theory states that dislocations keep piling up at the grain boundary till the resulting stress concentration is sufficient to activate slip systems in the adjacent grains. [88]. It has been observed that the degree of grain size hardening is dependent on the
material’s Hall-Petch coefficient and the extent of grain size refinement possible in materials [91].

Addition of solute atoms can be another way to increase the strength of a material. Solid solution strengthening increases the yield strength of crystalline materials due to the interactions between solute atoms and the dislocation movement. Introduction of solute atom into a crystal produces distortion in the lattice, resulting in a symmetric stress field around the solute [92]. The interaction of these stress fields with the dislocation leads to solute atom-dislocation interaction energy. Depending on the size of the solute atom, this interaction energy can be negative (solute atom size is smaller than solvent) or positive (solute atom is bigger than the solvent atom) [92].

Another potent source of strengthening can be the dispersion of second phase particles in the matrix, and is known as particle hardening. Particle strengthening can increase the strength markedly even with small volume fraction of dispersed particles as particles (aggregate of solute atoms) can resist dislocation penetration to a greater extent than individual solute atoms [93]. The amount of strengthening provided by particle strengthening depends on various factors like particle size, particle shape, volume fraction and nature of interface between particle and the matrix. These particles can affect the movement of dislocations in two different ways. The smaller coherent and/or softer precipitates tend to hinder the dislocation motion by particle shearing, where as larger incoherent particles cause dislocation bowing, also known as Orowan looping. The transformation from shearing to bowing takes place when the stress required for dislocation bowing becomes less than that required for shearing [92].
Figures 2-3 and 2-4 describe the mechanisms of particle shearing and Orowan looping respectively.

Even though having more strengthening mechanisms in a system can lead to higher strength, this study will be focused only on the solid solution strengthening due to the concerns about microgalvanic effect of precipitates and dispersoids [17, 65]. The grain boundary effect will inevitably be present due to different grain refining abilities of different alloying additions, and will be discussed later chapters.

2.3 Summary

Different aspects of corrosion, oxidation and strength of Mg alloys were discussed in this chapter. The thermodynamic driving forces for the corrosion and oxidation were mentioned. Various structure property relationships were also analyzed and the ones important to this study were identified.
Table 2-1. Chemical potential of Mg and its compounds in different states at 25°C

<table>
<thead>
<tr>
<th>Species</th>
<th>Oxidation State</th>
<th>State</th>
<th>$\mu_o$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0</td>
<td>Solid</td>
<td>0</td>
</tr>
<tr>
<td>Mg$^+$</td>
<td>+1</td>
<td>Ion</td>
<td>-61</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>+2</td>
<td>Ion</td>
<td>-109</td>
</tr>
<tr>
<td>Mg(OH)$_2$</td>
<td>+2</td>
<td>Solid</td>
<td>-199</td>
</tr>
<tr>
<td>MgH</td>
<td>-1</td>
<td>Gas</td>
<td>+34</td>
</tr>
<tr>
<td>MgH$_2$</td>
<td>-1</td>
<td>Solid</td>
<td>-8</td>
</tr>
<tr>
<td>MgO</td>
<td>+2</td>
<td>Solid</td>
<td>-136</td>
</tr>
</tbody>
</table>

[Adapted from Song, G. 2011. Corrosion of magnesium alloys (Page 5, Table 1.1). Woodhead Publishing Limited, Cambridge]

Table 2-2. Summary of literature related to the effect of changes in grain size on the corrosion susceptibility of Mg alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>Environment</th>
<th>Grain Size Range</th>
<th>Effect of grain size reduction on Corrosion Susceptibility</th>
<th>Processing Route</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ31B</td>
<td>3.5%NaCl</td>
<td>6 μm to 25 μm</td>
<td>Decreases</td>
<td>HT, SPD (FSW)</td>
</tr>
<tr>
<td>Mg-Y-RE-Zr</td>
<td>3.5%NaCl + Mg(OH)$_2$</td>
<td>≈25 μm</td>
<td>Decreases</td>
<td>HT</td>
</tr>
<tr>
<td>Mg (99.9%)</td>
<td>0.1 M NaCl</td>
<td>2 μm to 875 μm</td>
<td>Decreases</td>
<td>HT, SPD (ECAP, SMAT)</td>
</tr>
<tr>
<td>Mg (99.9%)</td>
<td>0.1 M NaCl</td>
<td>2 μm to 875 μm</td>
<td>Decreases</td>
<td>HT, SPD (ECAP, SMAT)</td>
</tr>
<tr>
<td>AZ91D</td>
<td>1 N NaCl</td>
<td>10 μm to 100 μm</td>
<td>Decreases</td>
<td>C</td>
</tr>
<tr>
<td>AZ91D</td>
<td>3.5% NaCl</td>
<td>≈15 μm to 100 μm</td>
<td>Decreases</td>
<td>C</td>
</tr>
<tr>
<td>AZ31</td>
<td>3.5% NaCl + Mg(OH)$_2$</td>
<td>3 μm to 35 μm</td>
<td>Decreases/Increases depending on processing</td>
<td>SPD (ECAP)</td>
</tr>
<tr>
<td>WE43</td>
<td>1% NaCl</td>
<td>0.5 μm to 15 μm</td>
<td>Increases</td>
<td>SPD (E, ECAP)</td>
</tr>
<tr>
<td>Mg (&gt;99.9%)</td>
<td>0.1 M NaCl</td>
<td>2.6 μm to 125 μm</td>
<td>Decreases</td>
<td>SPD (ECAP)</td>
</tr>
</tbody>
</table>

(HT-heat treatment, SPD-severe plastic deformation, FSW-friction stir welding, ECAP-equal channel angular pressing, SMAT-surface mechanical attrition treatment, C-casting) [Adapted from Ralston K.D and Birbilis N. 2010 Effect of grain size on corrosion: A review. Corrosion Vol. 66 Issue 7 (Page 075005, Table 1)]
Figure 2-1. Electrochemical force series [Reprinted with permission from John Wiley and Sons, 1999. Advanced Engineering Materials Vol. 1 (Pages 11-33, Figure 3)]
Figure 2-2. Schematic illustrations of the main aspects of metal-oxygen reactions and surface oxide growth. The figures show the initial adsorption of oxygen on the surface, followed by nucleation of oxide and its growth and the scale growth by solid-state diffusion. It is also shown that cracks and porosity in the oxide scale can lead to direct contact of the air with the substrate, thereby undermining the protective nature of oxide.
Figure 2-3. Schematic diagram of a dislocation cutting through a particle.

Figure 2-4. Schematic diagram of a dislocation passing between widely spaced precipitates based on Orowan’s bowing mechanism.
CHAPTER 3  
DESIGN APPROACH

3.1 Current Trends in Biodegradable Magnesium Alloy Development

A brief overview of the current trends in the research on biodegradable Mg alloys shows that there has been a significant increase in research and development in this field. However, a more detailed analysis of these trends shows that the majority of the initial research in the area was focused on the behavior of commercial alloys that were initially designed for non-biological applications like automobile and aerospace. A significant amount of work can be found on Al-Zn [94-97] and rare earth alloying additions [35, 98-100]. The alloying elements were primarily selected for their ability to increase their mechanical properties as well as their corrosion resistance. Thus at the time of their development, the biocompatibility of these alloying elements were not considered.

Although the preliminary in-vitro and in-vivo studies have not shown adverse toxicity, previous studies on alloying additions like Al and rare-earth elements have shown them to be toxic. It is therefore important to design alloys targeted towards specific applications, keeping in mind all the properties required for the optimal performance in their working environment. This chapter details the design approach utilized to develop new alloys that will be discussed later in this body of work.

3.2 Systems Design Approach

A system can be defined as a group of components that work coherently to achieve a certain goal and are often described by their complexity, hierarchy and multiple levels of inter-related subsystems [101, 102]. Based on this classification, materials inherently fall in the category of systems, as they have different components
like matrix, secondary phases and surface films etc. that interact at the subsystem level in a hierarchical fashion to output a required performance. This systems-based approach [103] can be applied to design and optimization of Mg-based biodegradable materials. The combination of a systems based design strategy grounded in materials science, where processing-structure-property relationships dictate and drive an overall performance, provides a methodology to strategically map the complex mechanistic relationships and understand their evolution from processing to performance [104].

Figure 3-1 shows a generalized systems design chart for development of Mg-based alloy for biodegradable applications. This chart identifies the performance requirements and then outlines the requisite property objectives required for achieving that performance goal. The characteristic microstructures that determine the property objectives are outlined in the structure column, which are then connected to the processing steps necessary for obtaining those structures.

The property column of the chart outlines the objectives required for the optimal performance of the material. Ashby’s methodology of material selection [105] can be a useful tool in clarifying these objectives as it helps us to identify the essential characteristics required for the desired application and comparing them with the available material set. This helps us in identifying the requirements that need to be fulfilled, and the consequent constraints on the material selection. The primary property requirements for biomaterials would be biocompatibility, corrosion resistance and strength. The systems design chart illustrates these properties in a hierarchal order, with the top tier having the highest weighting factor. After outlining the property objectives, the underlying microstructural subsystems that control these properties are
identified. In a system, different subsystems can have different and often contradictory effect on the required properties. An exhaustive and detailed listing of microstructural subsystems is therefore necessary for proper estimation of the final properties. Finally, the processes required for driving the microstructural development is listed in a sequential manner. Interlinks connecting the different subsystems identify the potential processing-structure or structure-property relationships. The latter of which are essentially physics-based models that can be supported by simulation or empirical modeling. Lastly, processing-structure relationships can be predicted using materials thermodynamics, enabling monitoring of microstructural evolution as a function of a particular processing condition.
Figure 3-1. Systems design chart for developing Mg-based biodegradable alloys
CHAPTER 4
DESIGN AND MICROSTRUCTURAL ANALYSIS OF BINARY MG-RE ALLOYS

4.1 Design of Binary Alloys

An optimal biodegradable implant material should be able to fulfill following essential requirements: (1) it should have sufficient strength to provide required structural support, (2) it should corrode slow enough to maintain the structural support and its mechanical integrity while the tissue is healing, and (3) it should corrode at a greater rate upon completion of tissue healing to prevent complications arising from long-term implant presence in the body.

These conditions have contrary microstructural requirements, and cannot be fulfilled using a homogenous alloy. Hence, to simultaneously satisfy all the requirements, the design methodology was focused towards developing a composite structure that has low initial degradation rate to maintain mechanical integrity until the tissue has healed and then have an increased dissolution rate to satisfy the third condition. Various methods of surface passivation have been investigated in literature, including polymer and ceramic coatings, microarc oxidation (MAO), plasma surface modification etc [18, 95, 106, 107]. However, these techniques often rely on either sophisticated machinery or additional chemical treatments of the alloys. Furthermore the fidelity of these surface coatings is precarious especially when coating devices with complex geometries. For this study, we are proposing to use a systems design approach to design an alloy microstructure that can form a passivating oxide on its surface when heated during the alloy processing, thereby eliminating the need for surface coating. This overall objective scheme is outlined in Figure 4-1. The proposed microstructural design has the benefits of eliminating the need of any complex
instrumentation or chemical treatments, thereby reducing the cost of material processing by designing a material that inherently self-passivates with a pre-determined scale that can demonstrate in-vitro stability.

4.1.1 Selection of Alloying Elements

4.1.1.1 Design considerations for surface oxide formation

Under normal atmospheric conditions, most of the metals react with their environment to form a thin layer of oxide or hydroxide on the surface. Altering or replacing the porous or non-protective surface layer with a protective one can significantly alter the reactivity of the surface. As discussed in Section 2.1.2, the native oxide on the surface of Mg under dry conditions is MgO, which can convert into a mixture of MgO and Mg(OH)$_2$ upon coming in contact with water. Since MgO is semi-protective, it does not provide sufficient protection against corrosion attack. To overcome the issue of non-protective surface oxide, Mg can be alloyed with other elements to achieve selective oxidation of the alloying element and replace MgO with more thermodynamically stable oxides.

The process of selective oxidation of the elements depends on the thermodynamics and kinetics of the system. Thermodynamically, the oxide with more negative $\Delta G_f$ has higher thermodynamic stability and will have a strong driving force to form preferentially. Additionally, the oxide with its P-B ratio closest to bulk material will have enhanced mechanical stability due to reduced mismatch between the oxide volume and the substrate volume. Figure 4-2 plots the $-\Delta G_f$ (negative Gibbs free energy of formation) values for the oxides of Mg alloying elements versus their molar volumes per mole metal [39]. The horizontal dotted line on the plot shows the energy of formation of MgO and the vertical line represents the molar volume of elemental Mg. Oxides to the
left of the vertical line have molar volume less than that of elemental Mg and will lack protection due to the porous nature of the oxide. The oxides below the horizontal dotted line are thermodynamically less stable than MgO and hence, will not form in presence of Mg. The arrow in the plot indicates the desired direction for the protective oxide, as the oxides too far to the right of vertical line can be prone to lack of mechanical stability due to compressive stress buildup. Based on these considerations, rare earth elements show promise of forming protective oxides, with Sc₂O₃ being the most promising among them. On the other hand, Zn, Li, Ca and Al can be eliminated as potential oxide forming elements due to the lower free energy of formation of their oxides and/or P-B ratio being less than 1.

Although the thermodynamic data provides us information about the stability of the oxides, the mobility of the cation and oxygen anion through the matrix and oxide dictates rate of oxide formation. Unfortunately, there is lack of kinetic data on the mobility and diffusivity of rare earth elements in Mg. To overcome this challenge, a systematic detailed experimental plan was created and executed to gain a deeper understanding of the role of solute and oxygen mobility on the growth kinetics of the surface oxide.

4.1.1.2 Design considerations for increasing strength by solution strengthening

Since low strength is one of the limitations of pure Mg, the design process was targeted towards obtaining higher strength of the alloy by introducing potent solute atoms to the Mg matrix. The maximum solid solubility of different alloying additions in Mg is mentioned in Table 4-1. It can be seen that Y, Sc and Gd show appreciable solid solubility range. Even though Ce and Mn fit the requirements for oxide formation as mentioned in previous section, they have very limited solubility, and hence have a low
potential for solid solution strengthening. Hence, they are not optimal choices for solid solution strengthening.

Since different alloying elements can have different amount of strengthening effect, an empirical model was used to predict the strengthening efficiency of different alloying elements. For dilute solid-solutions, Fleischer [108] developed a model based on the elastic interaction of screw and edge dislocations with the solute atoms, and calculated the relationship between solute concentration \( c \) and increase in resolved shear stress \( \Delta \tau \) as

\[
\Delta \tau \propto c^{1/2}
\]

The statistical theory of Fleischer was modified by Labusch [109] by using a statistical treatment of solute interactions with dislocations, and calculated the relationship between concentration and shear strength as

\[
\Delta \tau \propto c^{2/3}
\]

The experimental verification of these theoretical models showed that either model can be used depending on the investigated system [110]. However, it was observed that the extrapolation of these models into concentrated alloys gave values lower than the actual strength. In concentrated Mg-Al and Mg-Zn alloys (>0.1 at%), it was observed empirically that the solid solution effect had a linear relationship with increase in strength [80, 81]. Similar model was prepared for different alloying additions and is shown in Figure 4-3.

Furthermore, it was proposed by Nembach [111] that the strengthening mechanisms can be superimposed:

\[
\tau_{\text{Total}} = \left[ \tau_{\text{Mg}}^k + \tau_{\text{SS}}^k + \tau_{\text{PPT}}^k \right]^{1/4}
\]

\[
\tau_{\text{Total}} = \left[ \tau_{\text{Mg}}^k + \tau_{\text{SS}}^k + \tau_{\text{PPT}}^k \right]^{1/4}
\]
where $\tau_{\text{Total}}$ represents the "total" strengthening and depends on the strength of pure Mg ($\tau_{\text{Mg}}^k$), the solid solution strengthening ($\tau_{\text{SS}}^k$) and the precipitation strengthening ($\tau_{\text{PPT}}^k$). The value of $k$ is derived empirically and typically lies between 1.0 and 2.0. Since we are not aiming for strength contribution from precipitation, that term of the equation can be eliminated from the model.

### 4.1.1.3 Design considerations for grain size reduction

As described in Section 2.1.3.3, reduction in grain size has been associated with reduction in degradation rate and increase in strength of Mg alloys [72]. One of the most common ways for grain refinement is the addition of foreign nucleants and/or alloying elements [112]. However, since this work is focused on solid-solution based alloys, the effect of solute on grain size reduction is given more attention than the effect of different nucleating agents. The effect of solute on grain refinement can be explained in terms of growth restriction factor (GRF), which can be calculated using binary phase diagrams using the following equation:

$$\text{GRF} = \sum_i m_i C_{o,i} (k - 1)$$  \hspace{1cm} (4-4)

where $m_i$ is the slope of the liquidus line, $k_i$ is the distribution coefficient and $C_{o,i}$ is the initial concentration of the element $i$. Lee et. al. calculated the GRF for some of the alloying elements and the values are shown in Table 4-2. Among the elements selected based on their oxide forming abilities, Sc had the highest GRF followed by Y [112].

### 4.1.2 Selection of Alloying Compositions

Based on their highly stable oxides, large solid solubility in Mg and grain refining capabilities, rare earths Gd, Y and Sc best fit the design parameters for alloying additions and were chosen for further investigation.
After selecting the alloying elements, the next step in the design process was to calculate the nominal compositions of these alloys. There were three main considerations while deciding the alloy compositions: 1) single-phase microstructure, 2) acceptable corrosion rate of the alloys and 3) minimum amount of alloying addition needed to form a protective selective oxide. In order to simplify the comparison and reduce the variables associated with the experiments, it was decided to have same amount of alloying additions in all three systems.

First, binary phase diagrams were used to investigate the solid solubility of the selected Mg-RE systems. Phase diagrams were calculated using PANDAT [113] and its proprietary Mg database PANMAG [114]. The Mg rich sections of Mg-Gd, Mg-Y and Mg-Sc alloys are shown in Figure 4-4. Mg-Gd system has the lowest solid solution solubility at 500°C (approximately 8.5 wt%). The temperature was chosen as 500°C as it is sufficiently below the eutectic temperature of Mg-Gd binary system to prevent any accidental liquification of eutectic due to any possible heating fluctuations in the furnace, and still sufficiently high to allow fast oxidation kinetics [115, 116]. This composition was used for the first iteration of composition selection. Mg-8wt%Gd alloy was prepared to check the possibility of achieving solid solution at this composition. Figure 4-5(a) shows the as-cast images of Mg-8Gd alloy. It can be seen that eutectic is present in the microstructure of the as-cast alloy. The alloy was then heat treated at 500°C for 48 hours and then quenched in water in an attempt to make it a single-phase alloy. Figure 4-5(b) shows the microstructure of Mg-8Gd alloy after this heat treatment. It can be seen that the second phase precipitates are still present in the microstructure. In another attempt to get rid of these precipitates, an even longer heat treatment was
carried out in an effort to provide sufficient time for dissolution of precipitates. Figure 4-5(c) shows the microstructure even after 150 hours of homogenization at 500°C. However, the precipitates are still present in the microstructure. Based on these heat treatments, it was concluded that the kinetics of homogenization are too slow to attain thermodynamic equilibrium during the heat treatment processes. It was therefore decided to lower the concentrations of RE additions than the maximum solid solubility shown by the phase diagrams.

Second consideration for composition selection was to keep a low degradation rate of the alloys. There has been limited amount of work on degradation properties of Mg-Gd and Mg-Y that could be used for guidance. Furthermore, Mg-Sc system lacks any corrosion data in literature. Liu et. al. investigated the degradation behavior of a series of binary Mg-Y alloys ranging from 2-7wt%Y in 0.1M NaCl solutions and concluded that the degradation rate increases with increase in Y content [117]. During electrochemical impedance spectroscopy (EIS) analysis, initial degradation behavior of Mg-2Y and Mg-3Y was similar to high purity Mg and they maintained low corrosion rate up to 24 hours after immersion. On the other hand, Mg-4wt%Y showed severe degradation after only 5 hours immersion, as shown in Figure 4-6 [117]. As a result, it was concluded that significant change in corrosion behavior and rate occurs when the Y concentration increases from 3wt% to 4wt% in an alloy.

Thirdly, it is important for the alloying additions to be sufficient in concentration for formation of a selective surface oxide. Due to the lack of data on diffusion of rare earth materials in Mg, it was not possible to theoretically calculate the amount of alloying additions needed for formation of protective rare earth oxides on the Mg alloy surface.
However, Wang et. al. investigated the oxidation behavior of four different Mg-Y alloys (Y = 0.82, 1.09, 4.31 and 25 wt%). They showed that there is a critical value of Y content above which, a dense and protective oxide can form. This value should be between 1.09 wt% and 4.31 wt% as Mg-1.09 wt%Y alloy shows linear oxidation behavior associated with non-protective oxide and Mg-4.31 wt%Y shows parabolic oxidation behavior associated with protective oxide formation.

Based on the above considerations, it was decided to have 3 wt% alloying additions in the binary alloys as they were predicted to be well within the solid solubility range, were below the threshold level at which aggressive corrosion starts [117] and above the threshold level at which protective oxide formation occurs [116].

4.2 Materials and Methods

4.2.1 Alloy Preparation

Mg-3 wt%Gd, Mg-3 wt%Y and Mg-3 wt%Sc alloys were made using pure Mg chips (99.98%) and respective Mg-RE master alloys made from pure Mg (99.98%), Y (99.9%), Sc (99.9%) and Gd (99.9%) (Sigma-Aldrich, St. Louis, MO). To minimize the oxidation during alloy preparation, the entire process of mixing, melting, and casting was performed under argon atmosphere in a sealed glove box fitted with a resistance-heating furnace, as shown in Figure 4-7. To prepare the master alloys, the raw materials were weighed and mixed in graphite crucibles and heated at 825°C for 1 hour. The melts were stirred once using graphite rod, poured into graphite molds and allowed to cool at room temperature. These master alloys were then used to make dilute binary alloys. The melting and casting process for desired binary alloys was similar to the one used for master alloys, except that the furnace temperature was maintained at 750°C. This two-step process was used to ensure homogenous mixing and accuracy of
composition. The composition of the alloys was analyzed using inductively coupled plasma (ICP-AES, PerkinElmer Optima 3200RL; Perkin Elmer, Waltham, MA). The nominal and actual compositions of binary Mg-RE alloys are listed in Table 4-3. The alloys were then encapsulated under vacuum in quartz tubes, homogenized at 500°C for 8 hours and quenched in water.

4.2.2 Microstructural Characterization

The samples for microscopic analyses were cut from the ingot using low speed saw (Allied Techcut 4; Allied High Tech Products, CA) and then polished up to 0.03 μm using colloidal silica. The polished samples were etched using acetic picral. The microstructure of the samples was investigated using light optic microscopy (LOM, Olympus PME3; Olympus Corporation, Tokyo, Japan) and scanning electron microscopy (SEM, JEOL JSM 6400; JEOL Ltd., Tokyo, Japan). Crystallographic phase identification was performed using X-ray diffraction (XRD, Philips APD 3720; Koninklijke Philips Electronics N.V., Amsterdam, Holland). Optical micrographs were analyzed using the Image-J software program and grain size measurements were made according to the lineal intercept method outlined in ASTM Standard E112 [118].

4.2.3 Hardness Testing

The samples for hardness testing were polished upto 0.03 μm using colloidal silica to eliminate the surface defects. The micro-hardness testing was performed using 300 gf load on the alloys for 15 s. Seven different measurements were taken for each sample and their average was used.

4.3 Results and Discussion

Figure 4-8 shows the optical micrographs of binary samples etched with acetic picral to reveal grain structure. It can be seen that Mg-3Y and Mg-3Gd grains show
directional solidification and have columnar grains as compared to Mg-3Sc, which has finer equiaxial grains. Average grain size of Mg-3Y, Mg-3Gd and Mg-3Sc was $1032 \pm 322 \, \mu m$, $864 \pm 230 \, \mu m$ and $119 \pm 6 \, \mu m$ respectively. The large standard deviation in the Mg-3Y and Mg-3Gd alloys is due to their direction solidification and difference in the longitudinal and transverse lengths of the grains. Mg-3Sc had more equiaxed grain, and hence small standard deviation. Even though no studies on grain refinement effects of binary Mg-Sc alloys has been found in literature, similar grain refining is seen with the addition of Zr to Mg alloys. Effects of Zr additions on the grain refinement of Mg and its alloys are well documented in literature [91, 119]. It is widely accepted that grain refinement by Zr takes place by peritectic mechanism where Zr particles first precipitate as Zr rich Mg and promote nucleation of primary Mg grains through peritectic reaction. This mechanism can be identified by the presence of at least one Zr-rich core in each grain of the alloy [91, 120]. However, recently it has also been shown that addition of Zr lower than the peritectic composition can also lead to grain refinement of Mg alloys [119, 121]. Additionally, $\alpha$-Zr has same crystal structure as Mg and similar lattice parameters, thereby making the un-dissolved particles also effective nucleation sites for Mg alloy. It is also proposed that for low Zr-additions (below peritectic composition), grain refinement is mainly caused by its high growth restriction effect during solidification [112]. Peritectic nature of Mg-Sc system, along with its hexagonal crystal structure and its lattice parameter being very similar to Mg, present a compelling reason to believe that the grain refinements in Mg-Sc alloys is of similar nature as Mg-Zr alloys. However, since the alloy composition was lower than the peritectic composition, and no cores were observed at the centre of grains, it's possible that the main contributor to
grain refinement was the growth restriction effect of Sc and not the peritectic mechanism.

The SEM images of solution treated Mg-3Sc, Mg-3Y and Mg-3Gd are shown in Figure 4-9. The microstructure consists primarily of α-Mg phase. No second phase particles were observed in Mg-3Y and Mg-3Sc alloys. A few Gd rich particles were observed in the microstructure and can be seen in Figure 4-9 (a). The XRD analysis was performed to get crystallographic information of the alloys and the plots are shown in Figure 4-10. These plots did not show any peaks associated with second phase in any of the alloys and only showed peaks associated with α-Mg. Vickers micro-hardness testing of solution treated alloys was also evaluated and the results are shown in Figure 4-11. Based on the strength model discussed in Section 4.1.1.2 and shown in Figure 4-3, the predicted relationships between the amount of solute and hardness value (HV) are:

For Mg-Gd system: \( HV = 3.1 \times \text{wt\%} + 29 \) (4-5)

For Mg-Y system: \( HV = 4.2 \times \text{wt\%} +29 \) (4-6)

For Mg-Sc system: \( HV = 1.7 \times \text{wt\%} + 29 \) (4-7)

The value 29 represents the hardness of pure Mg as can be seen in Figure 4-11. Substituting the amount of solutes present in the alloys under investigation, the predicted hardness values are 39, 41.2, and 34 HV for Mg-3Gd, Mg-3Y and Mg-3Sc alloy respectively. The experimental values for these alloys are 44.1±5.2, 41.7±3.2 and 42.4±2.0 respectively. It can be seen that for Mg-3Gd and Mg-3Y, the experimental and calculated values are within one standard deviation of the each other. The experimentally obtained value for Mg-3Sc is significantly higher than the predicted
value. This could possibly be due to the higher amount of grain refinement in this alloy as compared to other alloys, thereby having greater grain boundary strengthening contribution in this alloy. Since the strength model does not include the grain boundary strengthening, it can lead to discrepancy in the predicted and actual strength values.

4.4 Summary

A systematic design methodology was proposed to develop an alloy system with the ability to self-passivate. Step by step analysis of property requirements was done and the microstructural features required for achieving those requirements were identified. Three different alloying elements were selected for their ability to show selective oxidation behavior, solid solution strengthening and grain refinement in Mg. Strength model to predict the strength of the designed alloys was developed and then experimentally verified.
**Table 4-1. Maximum solid solubility of different alloying elements in Mg**

<table>
<thead>
<tr>
<th>Alloying Element</th>
<th>Maximum Solubility (wt%)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>12.5</td>
<td>437</td>
</tr>
<tr>
<td>Scandium</td>
<td>24.6</td>
<td>710</td>
</tr>
<tr>
<td>Yttrium</td>
<td>11.4</td>
<td>587.4</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>23.49</td>
<td>548</td>
</tr>
<tr>
<td>Cerium</td>
<td>0.52</td>
<td>592</td>
</tr>
<tr>
<td>Calcium</td>
<td>1.34</td>
<td>516.5</td>
</tr>
<tr>
<td>Zinc</td>
<td>6.2</td>
<td>340</td>
</tr>
<tr>
<td>Manganese</td>
<td>2.2</td>
<td>650</td>
</tr>
</tbody>
</table>

**Table 4-2. Slope of liquidus line (m), Equilibrium distribution coefficient (k) and growth restriction parameter m(k-1) for different alloying elements in Mg**

<table>
<thead>
<tr>
<th>Element</th>
<th>m</th>
<th>k</th>
<th>m(k-1)</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>-12.67</td>
<td>0.06</td>
<td>11.94</td>
<td>Eutectic</td>
</tr>
<tr>
<td>Zn</td>
<td>-6.04</td>
<td>0.12</td>
<td>5.31</td>
<td>Eutectic</td>
</tr>
<tr>
<td>Al</td>
<td>-6.87</td>
<td>0.37</td>
<td>4.32</td>
<td>Eutectic</td>
</tr>
<tr>
<td>Sc</td>
<td>4.02</td>
<td>1.99</td>
<td>3.96</td>
<td>Peritectic</td>
</tr>
<tr>
<td>Sr</td>
<td>-3.53</td>
<td>0.006</td>
<td>3.51</td>
<td>Eutectic</td>
</tr>
<tr>
<td>Ce</td>
<td>-2.86</td>
<td>0.04</td>
<td>2.74</td>
<td>Eutectic</td>
</tr>
<tr>
<td>Y</td>
<td>3.40</td>
<td>0.50</td>
<td>1.70</td>
<td>Eutectic</td>
</tr>
</tbody>
</table>


**Table 4-3. Nominal and actual compositions of binary Mg-RE alloys**

<table>
<thead>
<tr>
<th>Nominal Compositions</th>
<th>Actual Compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-3 wt% Gd</td>
<td>Mg-3.2 wt% Gd</td>
</tr>
<tr>
<td>Mg-3 wt% Y</td>
<td>Mg-2.9 wt% Y</td>
</tr>
<tr>
<td>Mg-3 wt% Sc</td>
<td>Mg-2.9 wt% Sc</td>
</tr>
</tbody>
</table>
Figure 4-1. Schematic representation of the desired structure and the relative degradation rates

Figure 4-2. The free energy of formation of various oxides versus their volume per mole of metal at 25°C
Figure 4-3. Solid solution strengthening model showing the relationship between hardness and concentration of solute present in the alloys.
Figure 4-4. Phase diagrams of the Mg rich region of Mg-Gd, Mg-Y and Mg-Sc binary alloys
Figure 4-5. Optical micrographs of Mg-8Gd alloy (a) As-cast (b) Homogenized at 500°C for 48 hours (c) Homogenized at 500°C for 150 hours
Figure 4-6. Polarization resistance versus immersion time plot for Mg-Y alloys, HP Mg and LP Mg during 24 hour immersion in 0.1 M NaCl [Reprinted with permission from Elsevier, 2010. Corrosion Science Vol. 52 Issue 11 (Pages 3687-3701, Figure 10)]
Figure 4-7. Glove box used for melting alloys under inert atmosphere
Figure 4-8. Optical micrographs of etched (a) Mg-3Gd, (b) Mg-3Y and (c) Mg-3Sc alloys

Figure 4-9. SEM micrographs of homogenized (a) Mg-3Gd, (b) Mg-3Y and (c) Mg-3Sc alloys
Figure 4-10. The XRD plots of homogenized Mg-3RE alloys
Figure 4-11. Experimental and calculated micro-hardness values of the binary Mg-RE alloys. Hardness value of pure Mg is also shown for comparison.
CHAPTER 5
CHARACTERIZATION OF THE OXIDATION BEHAVIOR OF BINARY MG-RE ALLOYS

5.1 Thermodynamic Calculations and Prediction of Possible Oxidation Behavior

Based on the alloying elements present in the binary alloys, following reactions can take place between the alloying elements and oxygen:

\[
2\text{Mg} + O_2(g) \rightarrow 2\text{MgO} \quad (5-1)
\]

\[
2\text{Gd} + \frac{3}{2}O_2 \rightarrow \text{Gd}_2\text{O}_3 \quad (5-2)
\]

\[
2\text{Y} + \frac{3}{2}O_2 \rightarrow \text{Y}_2\text{O}_3 \quad (5-3)
\]

\[
2\text{Sc} + \frac{3}{2}O_2 \rightarrow \text{Sc}_2\text{O}_3 \quad (5-4)
\]

The Gibbs free energies (\( \Delta G_i \)) of these reactions at oxidation temperature (500°C) are -522.0 kJ, -1,675.4 kJ, -1,682.8 kJ and -1,583.9 kJ respectively. This shows that all the oxides have thermodynamic driving force for formation at the experimental conditions.

In addition to these reactions, rare-earth oxides can be formed by reduction of MgO. These reactions can be described as:

\[
2\text{Gd} + 3\text{MgO} \rightarrow \text{Gd}_2\text{O}_3 + 3\text{Mg} \quad (5-5)
\]

\[
2\text{Y} + 3\text{MgO} \rightarrow \text{Y}_2\text{O}_3 + 3\text{Mg} \quad (5-6)
\]

\[
2\text{Sc} + 3\text{MgO} \rightarrow \text{Sc}_2\text{O}_3 + 3\text{Mg} \quad (5-7)
\]

Under the experimental conditions, Gibbs free energy (\( \Delta G_i \)) can be approximately calculated using available thermodynamic parameters as [39]:

\[
\Delta G_i = \Delta G_i^0 + RT \ln \frac{a_{\text{Mg}}^3}{a_{\text{RE}}^2} \quad (5-8)
\]
where $\Delta G^0_T$ is the standard Gibbs free energy of the reaction at temperature $T$, $a_{Mg}$ is the activity of Mg and $a_{RE}$ is the activity of respective rare earth metal. For simplification, the activities of the Mg, Gd, Y and Sc were replaced by their molar atomic concentrations and the activity of oxygen was replaced by its volume fraction, which is equal to 1 as pure oxygen was used for oxidation. Hence, the activity values for different constituents of the selected systems are:

- For Mg-3Gd, $a_{Mg} = 0.9949$, $a_{Gd} = 0.0051$ and $a_{O_2} = 1$;
- For Mg-3Y, $a_{Mg} = 0.9929$, $a_{Y} = 0.0081$ and $a_{O_2} = 1$;
- For Mg-3Sc, $a_{Mg} = 0.984$, $a_{Y} = 0.016$ and $a_{O_2} = 1$;

Substituting the values in Equation 5-8, we get

$$\Delta G^Gd_{500} = 49.9 \text{ kJ}$$  \hspace{1cm} (5-9)

$$\Delta G^Y_{500} = -55.0 \text{ kJ}$$  \hspace{1cm} (5-10)

$$\Delta G^{Sc}_{500} = -56.5 \text{ kJ}$$  \hspace{1cm} (5-11)

These calculations reveal that even though Y and Sc will reduce the MgO and form their respective oxides, whereas Gd will not be able to reduce MgO. Based on these calculations, it can be predicted that binary Mg-Gd alloy will have an oxide layer constituting both MgO and Gd$_2$O$_3$, whereas Mg-Sc and Mg-Y alloy will have oxide layers constituting predominantly of Sc$_2$O$_3$ and Y$_2$O$_3$ respectively.

### 5.2 Materials and Methods

The samples for oxidation analysis were cut from the as cast ingots of Mg-3Gd, Mg-3Y and Mg-3Sc. They were then encapsulated in Pyrex tubes under vacuum and solution treated at 500°C for 8 hours. Rectangular samples with nominal dimensions of 9.5 mm × 9.25 mm × 1.3 mm were cut from the solution treated ingots. A hole was
drilled through the samples to facilitate the use of quartz hooks for hanging them in the thermo-gravimetric analyzer (TGA, Setsys Evolution TGA-DTA/DSC, SETARAM Inc., Hillsborough, NJ). This method was selected over using alumina pans for holding the sample because it reduces the buoyancy and/or drag from flow of O₂ through the specimen chamber. The samples were polished successively on emery papers of grit size 320, 600, 1200 and 4000, then cleaned and degreased ultrasonically in ethanol. To minimize the amount of oxide formed on the surface during room temperature exposure, the polished samples were placed in TGA immediately after degreasing in ethanol. The samples were inserted into the chamber at room temperature and heated to 500°C at 20°C/min under vacuum. The ramping up of temperature was carried out under vacuum to prevent any oxidation during the ramp up. Once the temperature reached 500°C, pure oxygen was introduced into the chamber at the rate of 196 ml/min. The samples were held isothermally at 500°C for up to 24 hours. The weight gain and temperature information was collected approximately every 17 seconds.

Analyses on the weight gain data obtained were performed to determine the kinetic parameters. The dimensions of the samples were assumed to be constant and change in the dimensions of the samples before and after the oxidation were ignored. Since the initial O₂ flow rate changes cause fluctuations in buoyancy, only the data after the stabilization of the O₂ flow rate was considered and any weight gain during the stabilization period was neglected.

The oxides on the samples were then characterized using XRD, SEM, auger electron spectroscopy (AES, Perkin Elmer PHI 660; Perkin Elmer, Waltham, MA) and x-ray photoelectron spectroscopy (XPS, Perkin Elmer PHI 5100 ESCA; Perkin Elmer,
Waltham, MA). SEM analysis was performed to analyze the surface characteristics of the oxides. XRD analysis was done using Cu Kα (λ=0.154 nm) radiation and a scanning rate of 0.8°/min for phase identification. AES was then used to obtain the depth profiles of the surface oxides. The operating voltage and current of the instrument was kept at 10 kV and 100 nA. A 3 kV argon beam was applied for sputtering and the sputter rate was estimated to be approximately 3.75 nm/min. Further, chemical analyses of the surface oxides were conducted using XPS. The instrument was operated at 15kV and 200 mA. Monochromated Al Kα (1486.6 eV) radiation was employed as an x-ray source and a 4 kV argon beam was used for sputtering.

5.3 Results and Discussion

5.3.1 Oxidation Kinetics of Binary Mg-RE Alloys

Long-term oxidation studies were performed on Mg-3Gd, Mg-3Y and Mg-3Sc alloys at 500°C in pure O₂ atmosphere. The weight gain versus time plot of the alloys is shown in Figure 5-1. The oxidation data shows that Mg-3Gd has the fastest oxidation rate and Mg-3Sc has the lowest oxidation rate. All the alloys show a high initial oxidation rate that reduces with time. A small amount of spalling was observed in Mg-3Y and Mg-3Sc that shows up as jumps/kinks in the weight gain versus time plots. As a result, only the data before spalling was used for calculation of oxidation kinetics.

Based on the TGA data, all the alloys show parabolic oxidation behavior in the long run. However, after looking at different regions of the TGA curve, it is observed that the oxidation behavior of Mg-3Gd and Mg-3Y comprises of 3 different regions: (A) fast initial oxidation (linear oxidation), (B) transition period, and (C) second oxidation regime following a parabolic oxidation mechanism. This behavior is illustrated in Figure 5-2,
which shows the plot of log $\Delta m$ (mass gain) versus log t (time) for Mg-3Gd. The general rate law for oxidation kinetics can be given by

$$\Delta m = kt^n + c$$  \hspace{1cm} (5-12)

where $k$ is the rate constant, $t$ is the time, $n$ is the time exponent of the rate law and $c$ is a constant. For linear kinetics, the value of $n$ is unity and for parabolic kinetics, the value of $n$ is 0.5. However, it has been shown by various researchers that metals and alloys show oxidation behaviors that deviate from the traditional linear, parabolic or logarithmic rate laws [123-126]. Often times, a combination of these laws can be seen in the oxidation behavior of a single material over a long period of oxidation.

It has been observed that a steady state parabolic oxidation is often preceded by a faster oxidation due to poor protective nature of initial oxide formed on the surface [45, 124]. Based on the log $\Delta m$ versus log t plots, the time exponent ($n$) of the fast initial oxidation of Mg-3Gd and Mg-3Y is 1.5 and 1.8 respectively. Pieraggi [45] suggests that when the initial oxide growth does not contribute to the steady state parabolic oxidation, it is beneficial to apply $\Delta m$ versus $t^{1/2}$ plot for evaluation of the parabolic rate law as compared to the $\Delta m^2$ versus $t$ plots as it helps in determination of true parabolic constant $k_p$. The plots of $\Delta m$ versus $t^{1/2}$ for the alloys are shown in Figure 5-3 and the values for the rate constants of the alloys are mentioned in Table 5-1. It can be seen that the fit of linear regression for the curves lies between 0.946 and 0.998. It is also observed that the oxidation rate of Mg-3Sc is 16 times lower than Mg-3Gd and 4 times lower than Mg-3Y, showing that Mg-3Sc forms a compact and protective oxide. However, this also implies that Mg-3Sc forms a thinnest oxide scale whereas Mg-3Gd forms the thickest scale.
5.3.2 Characterization of Surface Oxides on Mg-RE Alloys

Figure 5-4 shows the XRD spectra of Mg-3Sc, Mg-3Y and Mg-3Gd alloys isothermally oxidized at 500°C. It shows presence of Sc$_2$O$_3$, Y$_2$O$_3$ and Gd$_2$O$_3$ in Mg-3Sc, Mg-3Y and Mg-3Gd alloys respectively. Additionally, peaks associated with α-Mg are observed in all the alloys. However, only Mg-3Gd shows the peaks for MgO and no such peaks were observed in Mg-3Y and Mg-3Sc.

To further characterize the oxide layers, AES was used to get depth profiles of the oxide layers. The AES depth profiles of alloys after 5 hours of oxidation are shown in Figure 5-5 and the thickness of the oxide layers is ≈750, ≈350 and ≈150 nm for Mg-3Gd, Mg-3Y and Mg-3Sc alloys respectively. This fact implies highest oxidation rate of Mg-3Gd and lowest oxidation rate of Mg-3Sc, which is in agreement with the TGA results presented in Figure 5-1. It is also observed that oxide profile of Mg-3Gd consists mainly of Mg and O with minor gadolinium contribution. This result further indicates the presence of MgO and Gd$_2$O$_3$ in the oxide layer of Mg-3Gd, which is also in agreement with the XRD analysis shown in Figure 5-4. To visualize the structure of the oxide, the cross-section of the oxidized samples was investigated using electron microscopy. Figure 5-6 shows the cross-sectional micrograph of Mg-3Gd. It can be seen that the oxide layer is non-uniform and consists of two different oxides, brighter Gd rich oxide and darker Mg rich oxide.

On the other hand, Figure 5-7 and Figure 5-8 show that the oxide layer on the Mg-3Y and Mg-3Sc was uniform along the surface. Additionally, the AES depth profile of these alloys is different from Mg-3Gd profile, as it consists of two different regions, with a thin outer region comprising of a mixture of Mg and RE oxide (labeled as “A” in Figure 5-5) and a thick RE rich oxide region (labeled as “B” in Figure 5-5). Though the
total thickness of the oxide layer varies on all the alloys, the thickness of outer layer of Mg-rich oxide is approximately 20-30 nm in these alloys. Similar results have also been observed in other Mg-RE containing alloys [115, 116]. To verify if the region A of the oxide layer was the initially formed native oxide, AES analysis was performed on polished alloys that were kept in air at room temperature. Figure 5-9 shows the AES profile of polished Mg-3Sc alloy. It can be seen approximately 30 nm thick Mg rich native oxide is present on the surface.

To account for the lack of MgO peak in the XRD spectra and better understand the outermost layer of the oxides, XPS analysis was performed. All the energy positions were first adjusted by comparing the binding energy of C 1s peak to that of the standard binding energy of 284.8 eV, to compensate for the charging effect in the XPS measurements. Figure 5-10 shows the XPS spectra of the oxidation layer in the binding range of 0-1250 eV for all three alloys oxidized at 500°C for 5 hours. It can be seen that the peaks of Mg, O, C and Ar exist in the spectra of all the alloys. Mg KLL Auger peaks are also visible in the region of 300-380 eV and correspond to the Auger signal of kinetic energies in the region of 1106-1186 eV [127]. Similarly, oxygen KVV Auger peaks around 980eV correspond to the kinetic energy of 506.7eV [128]. Figure 5-10(a), (b) and (c) contain XPS peaks of Gd, Y and Sc in their respective spectra.

High-resolution XPS spectra for Mg 1s, O 1s and Gd 3d are shown in Figure 5-11. The Mg 1S peak shown can be attributed to the MgO and fits well with the standard [129]. Gd 4d peak for shown in Figure 5-10 is in agreement with the standard energy peak for Gd₂O₃, showing that the Gd present in the outer layer is in the form of Gd₂O₃ [130]. Oxygen1s is composed of two components with peaks at 529.6 and 531.7 eV.
The binding energy of 529.6 eV corresponds with the peak for MgO [131] while the other one can be attributed to Gd$_2$O$_3$ [132].

The XPS spectrum for Mg-3Y is shown in Figure 5-12. The Mg 1s peak is similar to that in Mg-3Gd, and corresponds to MgO [129]. Y 3d peak can be fitted with two sets of doublets, corresponding to Y 3d$_{3/2}$ and Y 3d$_{5/2}$ spin orbit splitting. The peak at 156.8 eV corresponds well with the standard value of Y 3d$_{5/2}$ peak of Y$_2$O$_3$ [133] while the peak at 158.8 eV is in agreement with the Y 3d$_{3/2}$ peak of Y$_2$O$_3$ [134]. This confirms the presence of yttrium in the form of oxide in the outer layer. The O 1s peaks at 529.8 and 531.7 further confirm the presence of MgO [131] and Y$_2$O$_3$ in the outer layer [135].

High-resolution images of Mg 1s and O 1s are shown in Figure 5-13. The Mg 1s peak is similar to ones seen in other alloys and corresponds to the MgO [129]. The O 1s peak can be deconvoluted into two peaks. The peak at 531.5 fits with the standard MgO peak [136], while the other one at 529.6 corresponds to Sc$_2$O$_3$ [137]. The presence of Sc$_2$O$_3$ in the outer layer is also supported by the presence of Sc 2p peak at 400.84 eV, which corresponds with the standard Sc$_2$O$_3$ peak [137].

### 5.4 Summary

The oxidation behavior of the Mg-3Gd, Mg-3Y and Mg-3Sc alloy was calculated using thermodynamics and validated by experimentation. It was shown that the thermodynamic calculations were able to correctly predict the composition and nature of the surface oxide scales on these alloys. Oxidation kinetics were investigated using TGA, and indicated that the alloys followed parabolic oxidation behavior, thereby forming protective oxide scales. The rate constants for oxidation were also determined and showed that Mg-3Sc formed the thinnest and most protective oxide whereas Mg-3Gd formed the thickest and least protective oxide. The oxides were characterized by
different characterization methods namely SEM, XRD, AES and XPS. It was observed that Mg-3Gd formed an oxide scale consisting of a mixture of MgO and Gd$_2$O$_3$, whereas Mg-3Y and Mg-3Sc had their oxide scales consisting exclusively of Y$_2$O$_3$ and Sc$_2$O$_3$ respectively.
Table 5-1. Parabolic rate constants for different alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature</th>
<th>Rate constant (mg/cm².s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-3Gd</td>
<td>500°C</td>
<td>$1.32 \times 10^{-7}$</td>
</tr>
<tr>
<td>Mg-3Y</td>
<td>500°C</td>
<td>$3.57 \times 10^{-8}$</td>
</tr>
<tr>
<td>Mg-3Sc</td>
<td>500°C</td>
<td>$7.71 \times 10^{-9}$</td>
</tr>
</tbody>
</table>
Figure 5-1. The isothermal TGA plots of Mg-3Gd, Mg-3Y and Mg-3Sc binary alloys at 500°C.

Figure 5-2. Kinetic parameters for Mg-3Gd for the 3 different oxidation regimes (A) linear oxidation (b) transition region and (c) parabolic oxidation.
Figure 5-3. Plots of $\Delta m$ versus $t^{1/2}$ for the alloys (a) Mg-3Gd, (b) Mg-3Y and (c) Mg-3Sc, showing long term parabolic oxidation behavior at 500°C.
Figure 5-4. The XRD plots of the alloys after isothermal oxidation at 500°C for 24 hours
(a) Mg-3Sc, (b) Mg-3Y and (c) Mg-3Gd
Figure 5-5. AES depth profiles of Mg-3Gd, Mg-3Y and Mg-3Sc oxidized isothermally at 500°C for 5 hours
Figure 5-6. SEM micrographs of the cross-section of oxidized Mg-3Gd alloy
Figure 5-7. SEM micrographs of the cross-section of oxidized Mg-3Y alloy
Figure 5-8. SEM micrographs of the cross-section of oxidized Mg-3Sc alloy

Figure 5-9. AES depth profile of polished Mg-3Sc alloy
Figure 5-10. XPS survey scan of entire binding energy for (a) Mg-3Gd (b) Mg-3Y and (c) Mg-3Sc

Figure 5-11. XPS spectra of Mg-3Gd oxidized for 24 hours
Figure 5-12. XPS spectra of Mg-3Y oxidized for 24 hours
Figure 5-13. XPS spectra of Mg-3Sc oxidized for 24 hours
CHAPTER 6
IN-VITRO DEGRADATION OF ALLOYS UNDER DIFFERENT SURFACE CONDITIONS

6.1 Materials and Methods

Magnesium degrades in physiological solutions according to the following reaction:

\[ Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \]  \hspace{1cm} (6-1)

The measurement of hydrogen evolved can be conveniently used to calculate the degradation rate of Mg alloys and has been extensively used in literature [68, 138, 139]. The samples for degradation studies were prepared from solution treated ingots of Mg-3Y, Mg-3Gd and Mg-3Sc alloys by cutting rectangular pieces of nominal dimensions 9mm x 9mm x 2mm using a low speed diamond saw. They were then polished up to 4000 grit surface finish using SiC emery papers. The polished samples were cleaned and degreased ultrasonically in ethanol. To analyze the effect of oxidation on the degradation behavior of samples, some of them were oxidized in pure O\(_2\) at 500°C for 24 hours. The apparatus used for immersion testing of both oxidized and non-oxidized alloy samples is shown in Figure 6-1. The immersion tests were carried out at 37°C in Hanks' balanced salt solution (HBSS) with composition of 0.185 g/l CaCl\(_2\).2H\(_2\)O, 0.40 g/l KCl, 0.06 g/l KH\(_2\)PO\(_4\), 0.10 g/l MgCl\(_2\).6H\(_2\)O, 0.10 g/l MgSO\(_4\).7H\(_2\)O, 8.00 g/l NaCl, 0.35 g/l NaHCO\(_3\), 0.48 g/l Na\(_2\)HPO\(_4\), 1.0 g/l D-Glucose (Thermo Scientific Inc., Waltham, MA) The ratio of surface area to the volume of the solution was held approximately 150 ml/cm\(^2\). The amount of hydrogen evolved and the change in pH was measured at 24 hour intervals. Due to the difference in the degradation rate and behavior of the alloys, degradation experiments were stopped at different times for each alloy. The two parameters used for ending the degradation experiments were:
1) if the amount of hydrogen released in 24 hours was more than the volume of the graduated cylinder used for measuring hydrogen evolved;

2) if there is visible disintegration of the pieces of sample due to corrosion, as it would affect the surface area.

After taking out the samples from Hanks' solution, they were washed with ethanol and then dried in air. Extreme care was taken to not remove any of the corrosion products formed on the surface of the samples. The corroded samples were characterized using XRD and SEM (JOEL 6335F FEG, JEOL Ltd., Tokyo, Japan) analysis. The XRD analysis was performed at 40 kV and 20 mA, with 2θ ranging from 20°-70° at the rate of 0.8°/min. The samples for SEM analysis were carbon coated prior to analysis to reduce the charging of deposited corrosion products.

6.2 Results and Discussion

Figure 6-2 shows the hydrogen evolution curves for the alloys in their oxidized and non-oxidized states obtained from immersion tests. Among non-oxidized samples, Mg-3Gd has the highest average degradation rate (≈4.5 ml/cm²/day) and Mg-3Sc had the lowest degradation rate (≈0.25 ml/cm²/day) after 48 hours. Hydrogen evolution measurement of Mg-3Gd was stopped after 48 hours, as the amount of hydrogen being evolved by the samples was more than the volume of the graduated cylinder used for measurement. For Mg-3Y and Mg-3Sc, it was seen that the rate of degradation increased with time. At the conclusion of the degradation analysis after 11 days, Mg-3Y had an average degradation rate of ≈4.95 ml/cm²/day while Mg-3Sc had an average rate of ≈1.01 ml/cm²/day.

The corrosion propagation was directly observed as a function of time for all the alloys. Figures 6-3, 6-4 and 6-5 show the optical micrographs of corrosion propagation on polished surfaces of the alloys. Upon immersion in Hanks' solution, corrosion started
at various points all over the surface for these alloys. All of the alloys showed some areas of uniform corrosion, pitting corrosion and filiform corrosion attack. Though the corrosion mechanisms involved looked similar, the aggressiveness and the propagation rate of each of the corrosion processes varied. Analysis of corrosion propagation with respect to time also supported the degradation analysis done using the hydrogen evolution studies. Mg-3Sc had the slowest corrosion propagation and showed only a small amount of pitting corrosion after 6 hours, with most of its surface being corrosion free. Mg-3Y had a little more corrosion attack after 6 hours, with some filiform and pitting corrosion occurring on the surface. On the other hand, Mg-3Gd showed the highest rate of corrosion and significant amount of pitting and filiform corrosion was seen on the surface. A large amount of degradation products were formed on its surface due to rapid degradation, which can be seen as cloudy grey areas in the optical images. It is also observed that the filiform corrosion predominantly starts from the edges of the samples and moves inwards, and can be seen in Figure 6-5. Similar observation was also made in other two alloys.

SEM analysis of the corroded surfaces further illustrated the corrosion mechanisms in the alloys. The micrographs of the alloys after 96 hours of immersion are shown in Figure 6-6, Figure 6-7 and Figure 6-8. It is observed that different types of corrosion are occurring simultaneously on all the alloy surfaces. Figure 6-6 shows the surface of Mg-3Sc. It can be seen that there are cracks in the surface layer (Figure 6-6b), presumably due to the volume change associated with conversion of MgO to Mg(OH)₂ [140]. Figures 6-6 (c,d) show the progression and morphologies of filiform corrosion. Figure 6-7 (b) shows the pitting corrosion in Mg-3Y. It was interesting to note
that a large area had surface cracks oriented in a single direction, showing the possible weakness of oxide/hydroxide along certain crystallographic planes, as shown in Figure 6-7(c). Figure 6-7(d) shows the tail of filiform corrosion with arrows marking the direction of propagation. It can be observed that the filiform corrosion in Mg-3Y is much more severe than in Mg-3Sc. Mg-3Gd had the most severe degradation and the surface of the samples was severely corroded after 96 hours. Figure 6-8 shows that its surface is full of deep cracks and valleys and a large amount of deposition of corrosion products can be observed. The corrosion products were also identified using XRD. The XRD plots of the alloys after 96 hours of immersion are shown in Figure 6-9. It can be seen that the XRD spectra show the presence of Mg(OH)$_2$ on all the samples.

To understand the corrosion mechanisms, it is essential to note that a spontaneous oxide/hydroxide film is formed on the surface of Mg and its alloys on exposure to air (native oxide) [54, 141], which has also been illustrated by XPS and AES analysis in previous chapter. The surface film is not necessarily compact and part of the substrate can be easily exposed to the solution. The addition of different alloying elements affects the properties and composition of this film. This is one of the reasons why different alloying elements have different effect on the reduction in degradation rate, as they can get incorporated into the surface film and change its protective properties. For Mg-Y alloys, it is known that Y can incorporate into the surface film in the form of Y$_2$O$_3$ and also as Y(OH)$_3$ in aqueous condition [98, 142]. Similarly, Gd$_2$O$_3$ has been found to be incorporated in surface film of Gd containing Mg alloys [115], and was also seen in the outer layer in Mg-3Gd described in previous chapter. Due to the presence of these semi-protective surface films, the degradation reactions on Mg mainly
occur at the bare parts of the substrate according to the following reactions [17, 143, 144]:

Cathodic reaction: \[ H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^- \] (6-2)

Anodic reaction: \[ Mg \rightarrow Mg^+ + 2e^- \] (6-3)

Chemical reaction NDE: \[ Mg^+ + H_2O \rightarrow Mg^{2+} + OH^- + \frac{1}{2} H_2 \] (6-4)

Overall reaction: \[ Mg + 2H_2O \rightarrow Mg^{2+} + OH^- + H_2 \] (6-5)

Corrosion product formation: \[ Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \] (6-6)

For Mg-3Gd, Mg-3Y and Mg-3Sc, following extra reactions can also occur during the degradation:

Anodic reactions:
\[ Gd \rightarrow Gd^{3+} + 3e^- \] (6-7)
\[ Y \rightarrow Y^{3+} + 3e^- \]
\[ Sc \rightarrow Sc^{3+} + 3e^- \]

Corrosion product formation:
\[ Gd^{3+} + 3(OH)^- \rightarrow Gd(OH)_3 \]
\[ Y^{3+} + 3(OH)^- \rightarrow Y(OH)_3 \]
\[ Sc^{3+} + 3(OH)^- \rightarrow Sc(OH)_3 \] (6-8)

Addition of Cl\(^-\) ions further aggravates the problem of localized degradation as they are smaller than hydroxide ions and can penetrate the surface film [17, 140, 145]. This can lead to the breakdown of its protective nature, leading to a more active corrosion on local sites, and can lead to pitting corrosion [117]. The formation of thicker oxide layers on the surface of the alloys can prevent this penetration of Cl\(^-\) ions by acting as a protective barrier. This is a possible explanation for the reduction in the degradation rate of oxidized samples as compared to the non-oxidized samples in the immersion tests. As shown in the section 5.2.2 of the previous chapter, Mg-3Y

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developed a compact and thick oxide layer on its surface, and showed the highest reduction in the degradation rate. On the other hand, Mg-3Sc had the thinnest oxide scale on the surface, and as a result showed the least amount of reduction in the degradation during the immersion testing. It is worthy to note that even though Mg-3Gd had the thickest oxide scale on the surface, it was non-uniform and bi-phase in nature. As a result, the protective nature of the surface oxide in Mg-3Gd was not as efficient as that of Mg-3Y.

For most of the metals, filiform corrosion is usually associated with coated surfaces and is driven by the oxygen reduction reaction [146]. However, filiform corrosion has been observed on uncoated Mg and various other Mg alloys in NaCl containing solutions[147]. Its presence indicates that there is a protective film on the surface of Mg, which is in agreement with our previous results. The classical method of filiform corrosion involving oxygen reduction reaction is not applicable in case of Mg and its alloys, as the cathodic reaction in these alloys is the generation of hydrogen [67, 77]. The propagation of filiform corrosion in Mg alloys is not yet completely understood and different mechanisms have been proposed to explain its behavior in Mg and its alloys. One of the proposed mechanisms is based on the acidification of filament tip due to the formation of hydrogen during degradation. According to this mechanism, Cl\textsuperscript{−} can penetrate the native oxide film on the surface due to its small size and attack the Mg substrate to form localized corrosion. This corrosion process leads to the release of H\textsuperscript{+} ions due to hydrolysis of Mg and other alloying elements present. This leads to the reduction of pH and acidification of the corrosion pits. These active sites act as the
filament tips and progress along the material, followed by a tail covered with degradation products [140].

An alternative mechanism attributes the filiform corrosion to the alkalization processes occurring at the bottom of the filiform attack. It assumes that during the initial localized corrosion, Mg(OH)$_2$ corrosion products are formed due to local pH increase. Additionally, the transformation of Mg to Mg(OH)$_2$ almost doubles the volume, resulting in filling of space in the localized cell. However, due to non-uniformity of the corrosion process, an active corrosion location is always present. As a result, a small active site is balanced with a large area of Mg(OH)$_2$, which acts as a cathode due to its high pH and passivates the surface. The active corrosion site always maintains a high concentration of Mg$^{2+}$, thereby attracting more Cl$^-$ ions and keeps the local site active [117]. In the present study, the initiation of the filiform corrosion from the sample edges indicates that the surface layer was less protective at the edges and it was easier for the Cl$^-$ ions to penetrate it. This reduction in protectiveness can be a result of sudden change in the crystal orientation of the grains at the edges, which can lead to non-uniformity or porosity in the oxide, thereby acting as preferential sites for filiform corrosion initiation.

Another important observation during the corrosion propagation investigation was that some of the grains were less susceptible to corrosion as compared to their neighboring grains, as shown in Figure 6-10. One of the possible reasons for this preferential corrosion can be the crystallographic orientation of the grains. Since Mg has an anisotropic crystal structure, it has different atomic density along different crystallographic planes. For Mg, basal plane (0001) has the highest atomic density, followed by (1\(\overline{1}2\)0) plane and then the (10\(\overline{1}0\)) plane [148, 149]. Since a close packed
plane has a higher atomic coordination, it has higher binding energy and lower surface energy. The surface energies ($E_s$) of (0001), (11\bar{2}0) and (10\bar{1}0) surfaces have been calculated to be 1.808, 2.156 and 1.868 eV/nm$^2$ respectively [150]. It is known that the electrochemical dissolution rate of a metal can be related to the activation energy ($Q$) required for a metallic ion to escape from the metal lattice and dissolve into the solution, and can be expressed as:

$$I_a = nFk \exp \left( \frac{Q + \alpha nE}{RT} \right)$$ (6-9)

where $n$ is the number of electrons involved in the electrochemical reaction, $k$ is a reaction constant, $\alpha$ is a transit coefficient, $F$ is Faraday constant, $R$ is the gas constant, $T$ is the absolute temperature and $E$ is the electrode potential, respectively. $Q$ is associated with the surface energy ($E_s$) according to the relation:

$$Q = Q_o - E_s$$ (6-10)

where $Q_o$ is a constant. If values of $\alpha$, $E$, $n$ and $k$ are same, the dissolution rates of different planes is dependent on their surface energy [149]. This can explain the preferential corrosion of some grains as compared to their neighbors.

6.3 Summary

The degradation behavior of the binary alloys was investigated in polished and oxidized conditions. Under polished conditions, Mg-3Sc has the lowest degradation rate, whereas Mg-3Gd has the highest degradation rate. Oxide scales led to varied amounts of reduction in the degradation rate. Mg-3Y was found to have the most protective oxide scale. It was observed that the corrosion propagation takes place by filiform and pitting corrosion. The initiation sites for filiform corrosion were predominantly
located at the sample edges. Additionally, the preferential degradation due to grain orientation was observed.
Figure 6-1. Experimental setup for measuring hydrogen evolution of samples

Figure 6-2. Hydrogen evolution rate of different oxidized and non-oxidized alloys
Figure 6-3. Optical micrographs of corrosion propagation in Mg-3Sc alloys (A) pitting corrosion (B) filiform corrosion

Figure 6-4. Optical micrographs of corrosion propagation in Mg-3Y alloys (A) pitting corrosion (B) filiform corrosion
Figure 6-5. Optical micrographs of corrosion propagation in Mg-3Gd alloys (A) pitting corrosion (B) filiform corrosion

Figure 6-6. SEM micrographs of Mg-3Sc alloy after 96 hours of degradation
Figure 6-7. SEM micrographs of Mg-3Y alloy surface after 96 hours of degradation
Figure 6-8. The SEM micrographs of Mg-3Gd surface after 96 hours of dissolution
Figure 6-9. XRD plots of Mg-RE binary alloys after 96 hours of immersion
Figure 6-10. Optical micrograph showing the selective corrosion of grains in Mg-3Y alloy. The grains marked “1” show relative passivity as compared to adjacent grains marked “2”
CHAPTER 7
INVESTIGATION OF THE OXIDATION AND DISSOLUTION BEHAVIOR OF TERNARY MG-SC-Y ALLOY

7.1 Design of Ternary Alloy

Evaluation of the binary systems provided useful information that can be used in deciding the next step in the design process. It was observed that no single alloying addition fulfilled all the desired design parameters. For example, although Gd was able to provide the thickest surface oxide scale, it was not homogenous. Sc was able to provide a fine grain size and low bulk degradation rate, but only produced a thin oxide layer that did not provide sufficient additional protection. On the other hand, Y additions were able to provide a compact and thick passivating oxide scale, but were not able to refine grains appreciably. Hence, as a next step to the design process, this chapter evaluates the design of a ternary alloy that incorporates the beneficial properties of two different alloying additions to achieve the design performance requirements.

Based on the previous chapters, Sc and Y were chosen as alloying additions. Gd was not selected because it was not able to provide homogenous surface oxide or grain refinement. Both Y and Sc were able to produce homogenous oxide scales, and Sc showed significant grain refinement. To further narrow down the range of Sc compositions, experimental investigation of its effect on grain size and degradation rate was conducted. Four Mg-Sc binary alloys with compositions of Mg-\(X\) Sc (\(X=0.5,1,2,3\)) were investigated. Figure 7-1 shows the reductions in grain size and degradation rate with increasing Sc additions. The addition of Sc to Mg reduces both the grain size and degradation rate. The increase in Sc concentration from 0.5 to 1 wt% shows the largest reduction in corrosion rate. Further additions show minimal reductions in degradation rate. On the other hand, increasing Sc concentration from 0.5 to 1 wt% shows no
change in grain size, but further increase leads to reduction in grain size. Based on these observations, 3 wt% Sc additions were chosen again as it showed the best properties out of all of the investigated alloys. The concentration of Y was kept at 3 wt% according to the design strategy described in Chapter 4.

Thermodynamic calculations to evaluate the oxidation behavior of the ternary system were performed as described in Section 5-1. Since no ternary interactions have been observed in the literature [115, 151], all the calculations were based on binary systems. The alloying elements present in the alloy can lead to the following oxidation reactions:

\[ 2Mg + O_2(g) \rightarrow 2MgO \]  \hspace{1cm} (7-1)

\[ 2Y + \frac{3}{2}O_2(g) \rightarrow Y_2O_3 \]  \hspace{1cm} (7-2)

\[ 2Sc + \frac{3}{2}O_2(g) \rightarrow Sc_2O_3 \]  \hspace{1cm} (7-3)

The Gibbs free energies (\(\Delta G_f\)) of these reactions at the oxidation temperature (500°C) are -522.0, -1,675.4, -1,682.8 and -1,583.9 kJ respectively. Additionally, it is known that the oxides with higher thermodynamic stability are able to reduce the oxides with lower stability. This leads to the possibility of following reactions:

\[ 2Y + 3MgO \rightarrow Y_2O_3 + 3Mg \]  \hspace{1cm} (7-4)

\[ 2Sc + 3MgO \rightarrow Sc_2O_3 + 3Mg \]  \hspace{1cm} (7-5)

Based on the relationship between the Gibbs free energy of these reactions, temperature and the activities of the constituents as described by equation below,

\[ \Delta G_{\tau} = \Delta G_{\tau}^c + RT \ln \frac{\alpha^3Mg}{\alpha_{RE}^3} \]  \hspace{1cm} (7-6)

the \(\Delta G_{500}\) values are:
\[ \Delta G^Y_{500} = -93.2 \text{ kJ} \quad (7-7) \]
\[ \Delta G^{Sc}_{500} = -89.2 \text{ kJ} \quad (7-8) \]

Hence, it can be seen that both \( \text{Sc}_2\text{O}_3 \) and \( \text{Y}_2\text{O}_3 \) have the thermodynamic driving force for simultaneous formation in the oxide scale.

Also, the experimental data from the binary alloys was added to the strength model shown in Section 4.1.1.2, to recalculate the relationship between amount of alloying additions and the resulting hardness increase. For the solution treated ternary alloy, the total hardness would be:

\[ HV = HV_{Mg} + \Delta HV^Y_{SS} + \Delta HV^{Sc}_{SS} \quad (7-9) \]

where \( HV \) is the total hardness of the alloy, \( HV_{Mg} \) is the hardness of pure Mg, \( \Delta HV^Y_{SS} \) and \( \Delta HV^{Sc}_{SS} \) are the solid solution strengthening contributions of Y and Sc respectively. Based on this model, the hardness value of the designed alloy was predicted to be 47 HV. Additionally, an empirical relationship was derived between hardness and yield strength by using the data from Gao et al. [152, 153]. A power law function was fit through the data as shown in Figure 7-2 and is represented as

\[ \sigma_y = 0.0022HV^{2.76} \quad (7-10) \]

where \( \sigma_y \) is the yield strength and HV is the Vickers hardness. Based on the predicted hardness value, the yield strength of the alloys was predicted to be 91 MPa.

7.2 Materials and Methods

Mg-3Sc-3Y alloy was prepared from pure Mg chips (99.98%) and the Mg-RE master alloys used for making binary alloys in previous chapters. The method and apparatus for melting and casting was also similar to the binary alloys. The composition of the alloy was analyzed using ICP-AES. The alloy ingot were encapsulated under
vacuum in quartz tubes, homogenized at 500°C for 8 hours and quenched in water. The samples for microscopic analyses were cut from the ingot, polished up to 0.03 μm using colloidal silica. The samples for grain size measurement were etched using acetic picral. Lineal intercept method outlined in ASTM Standard E112 [118] was used for grain size measurements. The microstructure characterization of the samples was investigated using optical microscopy, SEM and XRD. For TGA analysis, rectangular samples were cut from the ingots, ground to 4000 grit and cleaned in ethanol. The clean samples were then oxidized in high purity oxygen in a tube furnace and weighed after 0.5, 1, 2, 3, 4, 5, 10, 15, 20 and 25 hours. Analyses on the weight gain data obtained were performed to determine the kinetic parameters. The dimensions of the samples were assumed to be constant, thus the dimensional changes before and after the oxidation were ignored.

The oxides on the samples were then characterized using XRD, SEM, AES and XPS. SEM analysis was performed to analyze the surface characteristics of the oxides. XRD analysis was done using Cu Kα (λ=0.154 nm) radiation and a scanning rate of 0.8°/min for phase identification. AES was then used to obtain the depth profiles of the surface oxides. The operating voltage and current of the instrument was kept at 10 kV and 100 nA. A 3 kV argon beam was applied for sputtering and the sputter rate was estimated to be approximately 3.75 nm/min. Further, chemical analyses of the surface oxides were conducted using XPS. The instrument was operated at 15 kV and 200 mA. Monochromated Al Kα (1486.6 eV) radiation was employed as an x-ray source and a 4 kV argon beam was used for sputtering.
Vickers microhardness testing was performed using 300 gf force for 15 seconds. Compression testing was performed at a strain rate of 6% min\(^{-1}\) using Instron 5582 universal testing machine.

**7.3 Results and Discussion**

ICP-AES analysis showed the actual composition of the alloy to be Mg-2.8Sc-3Y. Figure 7-3 shows the optical images of solution treated Mg-3Sc-3Y alloy. It can be seen that the microstructure has fine, equiaxed grains with an average grain size of 109 μm. The XRD analysis of this alloy is shown in Figure 7-4. It can be seen that XRD spectra consists of peaks of α-Mg only, and no peaks related to secondary phases were found. However, the SEM analysis of the microstructure did reveal some second phase particles. To identify the constituents of this phase, EDS was done on the samples. Figure 7-5 shows the SEM micrograph of the microstructure along with the EDS plot and elemental maps. It can be seen that the second phase particles present are Y-rich binary phase. Based on the elemental analysis, binary phase diagram and the morphology of the particles, they can be identified as Mg\(_{24}\)Y\(_5\) phase particles. It can also be seen that Sc is evenly distributed throughout the matrix and no Sc rich secondary phase is present. This also means that there is a higher amount of Sc present in the solid solution as compared to Y, as some of the Y is stored in the second phase precipitates.

Figure 7-6 shows the thermo-gravimetric analysis of the alloy at 500°C. The oxidation behavior of the alloy is parabolic in nature, with a higher initial rate of oxidation associated with the adsorption of oxygen and initial scale formation, followed by slow oxide growth [44]. The parabolic behavior of the oxide growth as a function of time growth can be fitted to the parabolic equation as:
\[ \Delta m = (k_p t)^{1/2} + c \] (7-11)

where \( \Delta m \) is the weight gain per unit area, \( k_p \) is the parabolic rate constant, \( t \) is the oxidation time and \( c \) is the constant [44]. The linear fit between the \( \Delta m \) and time \( t^{1/2} \) was used to calculate the rate constant and is shown in Figure 7-7. The parabolic rate constant for Mg-3Sc-3Y at 500°C is \( 5.57 \times 10^{-8} \) mg/cm\(^2\)/s and is close to that of binary Mg-3Y (3.57 \times 10^{-8}) and about an order of magnitude higher than Mg-3Sc (7.71 \times 10^{-9}).

Figure 7-8 shows the SEM micrographs of the oxide cross-section and shows a thick and compact surface oxide. XRD analysis showed presence of both Sc\(_2\)O\(_3\) and Y\(_2\)O\(_3\) and is shown in Figure 7-9. To further understand the relative positions of binary oxides in the scale, AES depth profiling was done on the alloys and is shown in Figure 7-10. It can be seen that the oxide structure of the oxide is similar to the two region profile described in section 5.2.3, with a thin outer Mg rich oxide layer and a thick inner RE oxide rich layer. It can be seen that both Sc and Y are present throughout the depth of the oxide scale. This is in agreement with the results of thermodynamic calculations described in Section 7.2. It is also observed that the concentration of Sc in the oxide is higher than that of Y. This shows that the oxide layer is has higher amount of Sc\(_2\)O\(_3\) than Y\(_2\)O\(_3\). This can be possibly due to higher Sc content in the solid solution as some of the Y was locked in second phase Mg\(_{24}\)Y\(_5\) particles (Figure 7-5).

XPS analysis was also performed on the samples to characterize the phases present in the outer layer of the oxide. All the energy positions were first adjusted by comparing the binding energy peak in the experimental spectra to that of the standard binding energy of 248.8 eV to account for the charging effect in the XPS measurements. The XPS spectrum of the oxide over the entire range of 0-1250 eV is shown in Figure 7-
11. It confirms the presence of Mg, O, Sc, and Y in the outermost layer. In addition to the XPS peaks, Mg KLL and O KLL Auger peaks are present in the spectrum in the regions of 300-380 eV and 1106-1186 eV [127].

High-resolution XPS spectral peaks for constituent elements are shown in Figure 7-12. The positions of the peaks are similar to those found in the binary alloys. The position of Mg 1s peak is 1304.4 eV, which corresponds to the standard Mg 1s peak for MgO. Y 3d peak can be split into a set of doublet peaks, corresponding to 3d_{3/2} and 3d_{5/2} spin orbital splitting and the peak at 157.7 aligns with the Y3d_{5/2} peak [130]. This confirms the presence of Y in the outer layer of the oxide as Y_{2}O_{3}. The Sc 2p peak was observed at 401.8 eV, which corresponds with Sc_{2}O_{3} peak reported in the literature [154]. Similarly, the deconvoluted peaks of O 1s correspond well with the peaks for MgO and Sc_{2}O_{3} [136, 137].

Degradation studies were performed on the oxidized and non-oxidized to evaluate the surface passivation properties of the oxide. The hydrogen evolution curves of the alloy surface with different treatments are shown in Figure 7-13. It can be seen that polished sample has a corrosion rate of approximately 1.1 ml/cm^2/day, which is comparable to that of the binary Mg-3Sc and lower than the rate of both binary Mg-3Gd and Mg-3Y alloys. It was observed that oxide layer formed by oxidation at 500°C for 5 hours led to the initial reduction in the degradation rate to 0.16 ml/cm^2/day. This rate was maintained up to 7 days, after which the degradation rate increased to that comparable of polished sample. This shows that the oxide layer provides protection from the degradation and once the oxide layer is corroded, the degradation rate jumps back to that of the bulk material. To see the effect of oxide thickness, samples oxidized
for 24 hours were immersed in Hanks' solution. The oxide layer on these samples was able to reduce the degradation rate to 0.01 ml/cm²/day for up to 23 days. This rate is lower than most of the commercially available Mg alloys and is comparable to that of high purity Mg [17, 68]. As shown in Figure 7-14, the XRD analysis of the corroded surfaces revealed the presence of Mg(OH)₂ on the surface. For non-oxidized surface, uniform corrosion with localized regions of pitting and filiform corrosion was observed. Figure 7-15 shows two different regions of the same sample. Figure 7-15(a) shows the area around a pit, which has higher amount of corrosion cracks and degradation products as compared to Figure 7-15(b). On the other hand, the SEM analysis of the surface of oxidized Mg-3Sc-3Y alloy samples after immersion shows no corrosion cracks or any pitting corrosion (Figure 7-16). The darker regions in the micrographs show that the formation of hydroxide on the surface has started, but is not yet complete.

The microhardness evaluation of the samples was performed to validate the strength model prediction. The measured value of Vickers hardness of the alloy was 48.5±3.9 HV. This calculated value was within half a standard deviation of the experimental value, showing a good predictability of the model. The experimental yield strength of the alloys was found to be 100±3.5 MPa. The experimental value of yield strength is higher than the predicted value, because it was based on predicted hardness values, which are lower than the experimental values. The comparison of the predicted and experimental hardness and strength values is shown in Figure 7-17.

7.4 Summary

Ternary Mg-3Sc-3Y alloy was designed based on thermodynamic calculations and the data obtained from the analysis of binary alloy systems. The oxidation kinetics were evaluated using TGA and the oxidation rate constant was determined. The
characterization of the oxide showed that the oxide layer consisted of Sc$_2$O$_3$ and Y$_2$O$_3$, which was in agreement with the thermodynamic calculations. It was also seen that the surface oxide scale was passivating in nature, and that increasing the oxidation time increased the passivating behavior of the oxide. It was shown that 24 hours of oxidation at 500°C was enough to passivate the surface for 23 days, thereby reducing the degradation rate to less than 0.01 ml/cm$^2$/day of hydrogen evolved during this period. Finally, the microhardness and compression testing showed that the modified strength model was able to predict the hardness and yield strength values with appreciable accuracy.
Figure 7-1. Effect of Sc additions on the grain size and the rate of hydrogen evolution in binary Mg-Sc alloys
Figure 7-2. Yield strength vs hardness data fitted to a power law to derive Equation 7-10

Figure 7-3. Optical micrograph of solution treated Mg-3Sc-3Y
Figure 7-4. XRD plot of Mg-3Sc-3Y alloy homogenized at 500°C for 8 hours
Figure 7-5. SEM micrographs showing elemental mapping and EDX plot of solution treated Mg-3Sc-3Y alloy
Figure 7-6. Plot showing the weight gain per cm$^2$ vs time

Figure 7-7. Plot showing the calculation of parabolic rate constant by plotting mass gain per cm$^2$ vs square root of time
Figure 7-8. SEM micrographs of the cross section of Mg-3Sc-3Y oxidized for 5 hours
Figure 7-9. XRD plot of Mg-3Sc-3Y alloy oxidized at 500°C for 5 hours

Figure 7-10. AES depth profile of Mg-3Sc-3Y alloy oxidized for 5 hours at 500°C
Figure 7-11. XPS survey of Mg-3Sc-3Y alloy oxidized for 5 hours
Figure 7-12. XPS multiplex peaks for Mg, O, Sc and Y, showing the presence of MgO, Sc$_2$O$_3$ and Y$_2$O$_3$ in the outermost layer of oxide scale of Mg-3Sc-3Y alloy
Figure 7-13. Hydrogen evolution behavior of Mg-3Sc-3Y alloy under different surface conditions
Figure 7-14. XRD plot of Mg-3Sc-3y (polished) alloy after 96 hours in Hanks’ solution
Figure 7-15. SEM micrographs showing the corroded surface of non-oxidized Mg-3Sc-3Y alloy (a) area of severe pitting corrosion (b) area of relatively low corrosion rate on the same sample
Figure 7-16. SEM micrographs of the corroded surface of 24 hour oxidized Mg-3Sc-3Y after 96 hours immersion in Hanks’ solution
Figure 7-17. The comparison between the predicted and experimental values of hardness and yield strength of Mg-3Sc-3Y alloy.
Mg alloys have the potential to be a viable alternative to the traditional metallic implants for temporary structural implant applications. However, some of the limitations like high degradation rate and low strength need to be overcome before they can play a competitive role as a biodegradable implant material. The focus of this research was to use a systematic thermodynamics based approach to design and develop new alloys with a potential for controlled degradation by self-passivation. A detailed analysis of property requirements for the design goal was described and the required microstructural features were identified.

Based on the design parameters, the oxide stability of the alloying elements and solid solution solubility were chosen to be the most important requirements for their selection. From the available pool of alloying elements, Gd, Sc and Y were selected due to the high thermodynamic stability of their oxides, >1.0 P-B ratio, high solid solution solubility and grain refining abilities. Additions of 3.0 wt% were chosen for binary alloys based on their respective phase diagrams and the effect of concentration on the oxidation and corrosion behavior. Additionally, hardness was used as a measure for strength and a model was developed to predict the strength of the alloys.

Microstructural analysis of the alloys showed that the processing steps were able to obtain the desired microstructure, with some minor deviations in Mg-3Gd alloy. It was also shown that the predicted values of hardness were within one standard deviation of experimental values for Mg-3Gd and Mg-3Y alloys. The values obtained were used to refine the model. Then based on the thermodynamic calculations, the oxidation behavior of the alloys was predicted. Additionally, insight into the kinetic behavior of the
oxide species was obtained using TGA to get a complete understanding of the oxidation process in these alloys. The oxidation behavior was analyzed and the oxides were characterized. It was found that Mg-3Gd alloy has the fastest oxidation kinetics and the thickest oxide scale, whereas Mg-3Sc had the slowest kinetics and the thinnest oxide scale. The SEM, AES and XPS analysis revealed that Mg-3Gd developed a non-homogenous oxide scale that comprised of MgO and Gd$_2$O$_3$. On the other hand, Mg-3Sc and Mg-3Y developed mostly homogenous oxide scales consisting of their respective RE$_2$O$_3$, with a thin outer layer rich in MgO. The oxidation behavior of the alloys was in agreement with the thermodynamic calculations.

In the next step, the degradation behavior of these alloys was investigated and the effects of different alloying additions as well as surface oxides were investigated. It was seen that Gd addition led to the highest degradation rate whereas Sc addition led to the slowest degradation rate. However, due to its low thickness, Sc$_2$O$_3$ did not provide any passivation. On the other hand, Y had a thick and uniform oxide layer, which showed the best passivation behavior among the three alloys. It was also observed that the corrosion propagation took place by similar mechanisms in all the alloys and differed only in the rate at which these reactions progressed.

Finally, all the information gathered from the binary alloys was used to design a ternary alloy with a mixed surface oxide consisting of Sc$_2$O$_3$ and Y$_2$O$_3$. Degradation analysis of oxidized and non-oxidized ternary alloy showed that the oxide scale was protective and 24 hour oxidation was able to passivate the surface for up to 25 days, after which the corrosion rate changed to match that of non-oxidized sample.
CHAPTER 9
FUTURE WORK

The current study used a systems design approach to select an alloy system, predict the structure property relationships and validate them with experimental analysis. It was observed that selective oxidation of alloying additions to Mg can be a potent way to control the initial degradation rate. Even though this study was able to fulfill its design goals, further work is needed to optimize the composition and the processing parameters to achieve better properties.

To improve the yield and ultimate strength of the alloy, additional mechanisms like precipitation strengthening should be added to the design approach and their effect on the strength should be investigated. An empirical model similar to the solid solution strengthening model presented in this work should be made and used to predict the relationship between alloying additions and precipitation strengthening contribution. However, presence of precipitates would also affect the degradation behavior of the alloy due to microgalvanic corrosion. Therefore, further studies are needed to find a balance between higher strength and low degradation rate.

Additionally, we saw a relationship between the oxidation time/oxide thickness and the surface passivity. The kinetic and degradation data obtained in this study can be combined with results from additional oxidation studies at different temperatures to understand the relationships between time, temperature, oxide thickness and the duration of surface passivity. These empirical relationships can help us control the passivity of surface oxide and predict the length of initial passivity of the material.

Finally, in order to for this work to reach its ultimate design goal of producing a completely biodegradable and biocompatible alloy with controlled and predictable
degradation, in-vivo analysis will be essential. They would aid in correlating the in-vitro and in-vivo results, thereby providing us with better insight into the material behavior in its actual working environment, as it is not possible to completely replicate the in-vivo conditions in-vitro. The in-vivo data for hydrogen evolution, toxicity of the ions and the mechanical stability of the alloys can then be used in next iterations of the design to improve the performance.
LIST OF REFERENCES


[34] Troitskii VV, Tshitrin DN. Khirurgiia 1944;8:41-44.


BIOGRAPHICAL SKETCH

Harpreet Singh Brar was born in 1984 in Bathinda, India. After completing his secondary school education in Bathinda, he moved to Chandigarh where he completed his senior secondary education from D.A.V. College. He earned his B.E in metallurgical and materials engineering from Punjab Engineering College (PEC) Chandigarh. In addition to academics, he also pursued several of his other interests like soccer and basketball. He then joined the Materials Science and Engineering Department at the University of Florida to pursue graduate studies. Here, he was introduced to design and development of magnesium alloys and went on to pursue a Ph.D. in this field.